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Supporting Information for

Amplification of weak chiral inductions for excellent control over the helical orientation of discrete topologically chiral $(M_3L_2)_n$ polyhedra

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1. Experimental procedure

1.1 General information

Melting points were determined on an MPA100 OptiMelt (Stanford Research System). High-resolution ESI-MS data were recorded on a Bruker maXis spectrometer (Instrument Center at Institute for Molecular Sciences (IMS), Okazaki, Japan) and a Waters Xevo G2-XS Q-Tof. Silica gel chromatography was carried out using Silicagel 60N (Kanto Chemical, neutral, spherical) or Biotage SNAP Ultra cartridge. Solvents and reagents were purchased from TCI, FUJIFILM WAKO Pure Chemical Industries, Sigma-Aldrich (Merck), Combi-Blocks and Kanto Chemical. Unless otherwise noted all of the chemicals were reagent grade and used without any further purification. Unless otherwise noted all the synthetic reactions were conducted in argon gas atmosphere. Circular dichroism (CD) spectra were measured on a JASCO J-720WI and a JASCO J1500 (Instrument Center at IMS) using a quartz cell (S15-UV-1, GL Sciences Inc.). UV-vis spectra were measured on a UV-1900 (SHIMADZU) using a quartz cell (S15-UV-1). MM calculations for illustrative molecular models were conducted using BIOVIA Material Studio Forcite (Dassault Systems).

NMR spectra were measured on spectrometers as below:

• JEOL JNM-ECZ700R (700 MHz, JEOL, Akishima, Japan) equipped with an inverse triple resonance cryogenic probe (UltraCOOL-HCN), for dimeric assembly **2b**

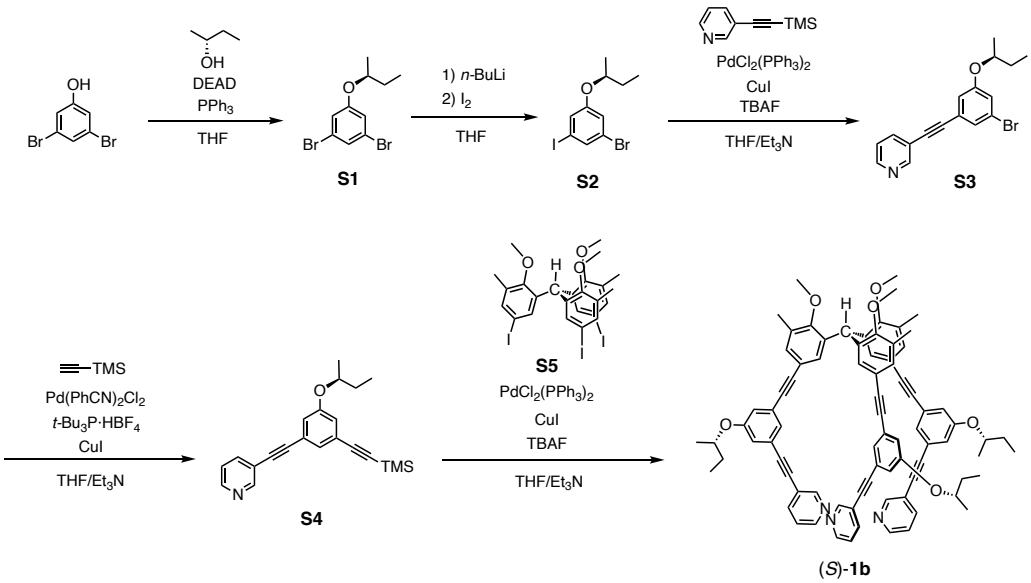
• Bruker Avance III HD (500 MHz) spectrometer equipped with a PABBO probe and Bruker AV-500 (500 MHz) spectrometer equipped with a CP-TCI cryoprobe, for small-molecule compounds and tetrahedral assembly **3b**

• Bruker AVANCE800 spectrometer (800 MHz, IMS) for cubic assembly **4b**

Abbreviations

DEAD: Diethyl azodicarboxylate
ESI-MS: Electrospray ionization mass spectroscopy
GC: Gas chromatography
HR-ESI-TOF-MS: High resolution ESI time of flight MS
M.p.: Melting point
NMR: nuclear magnetic resonance
TBA: Tetrabutylammonium
TBAF: Tetrabutylammonium fluoride
THF: Tetrahydrofuran
TMS: Trimethylsilyl
TMA: Tetramethylammonium
rt: room temperature

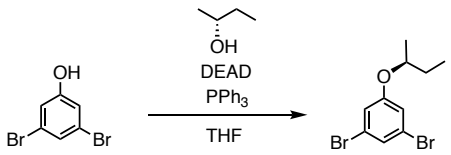
1.2 Synthesis of ligand (*S*)-1b



Triiodide **S5** was prepared according to the procedure previously reported.[S1,S2]

Unless otherwise noted, (*S*)-isomers of ligand **1b-e** were used for studies in the main article. That is why they are described just as "**1b-e**" there.

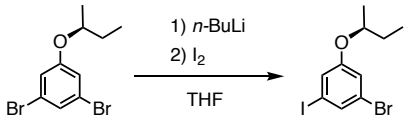
Synthesis of (*S*)-1-(*sec*-butoxy)-3,5-dibromobenzene S1



A solution of 3,5-dibromophenol (2.27 g, 9.01 mmol), (*R*)-2-butanol (0.75 mL, 8.18 mmol) and triphenylphosphine (2.38 g, 9.07 mmol) in THF (30 mL) was cooled to 0 °C. To the solution was slowly added DEAD (4.8 mL, 10.6 mmol in toluene). After the mixture was stirred at room temperature overnight, it was stirred furthermore at 40 °C for 1 h. After evaporation, the residue was diluted with *n*-hexane and filtered to remove triphenylphosphine oxide. After further dilution with dichloromethane, the organic layer was washed with saturated NaOH aq. and brine. The organic layer was concentrated *in vacuo*, and the residue was purified by silica gel column chromatography (hexane) to give **S1** (2.30 g, 83%) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 7.21 (s, 1H), 6.97 (d, J = 1.4 Hz, 2H), 4.28-4.22 (m, 1H), 1.76-1.67 (m, 1H), 1.66-1.57 (m, 1H), 1.28 (d, J = 6.1 Hz, 3H), 0.96 (t, J = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ 159.55 (C), 126.03 (CH), 123.08 (C), 118.04 (CH), 75.94 (CH), 29.01 (CH_2), 19.01 (CH_3), 9.65 (CH_3); GC-MS: *m*/*z* calcd. for $C_{10}H_{12}Br_2O$: 307.92 ($^{79}Br^{81}Br$), 305.93 ($^{79}Br_2$), 309.92 ($^{81}Br_2$) ([M]$^+$); found: 307.9, 305.9, 309.9.

Synthesis of (*S*)-1-bromo-3-(*sec*-butoxy)-5-iodobenzene S2

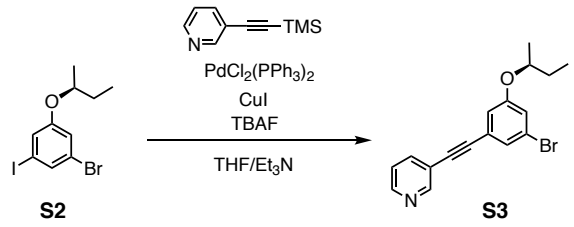


S1 **S2**

A solution of (*S*)-1-(*sec*-butoxy)-3,5-dibromobenzene **S1** (2.21 g, 7.14 mmol) in dehydrated THF (50 mL) was cooled to –78 °C, and *n*-BuLi (2.85 mL, 2.8 M in *n*-hexane) was added dropwise. After the mixture was stirred at –78 °C for 1 h, a solution of I_2 (3.63 g, 14.3 mmol) in THF (10 mL) was added, and the mixture was furthermore stirred at –78 °C for 1 h. After the reaction mixture was warmed up to room temperature over 30 min, the reaction was quenched by Na_2SO_3 aq. After evaporation of THF, the residue was diluted with dichloromethane and washed with brine. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane) to give (*S*)-1-bromo-3-(*sec*-butoxy)-5-iodobenzene **S2** (2.35 g, 92%) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 7.40 (s, 1H), 7.16 (s, 1H), 6.99 (s, 1H), 4.27-4.21 (m, 1H), 1.75-1.67 (m, 1H), 1.65-1.57 (m, 1H), 1.27 (d, J = 6.1 Hz, 3H), 0.96 (t, J = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ 159.35 (C), 131.66 (CH), 123.96 (CH), 123.11 (C), 118.72 (CH), 94.21 (C), 75.88 (CH), 29.02 (CH_2), 19.01 (CH_3), 9.66 (CH_3); GC-MS: *m*/*z* calcd. for $C_{10}H_{12}BrIO$: 353.91 (^{79}Br), 355.91 (^{81}Br) ($[M]^+$); found: 353.9, 355.9.

Synthesis of (*S*)-3-((3-bromo-5-(*sec*-butoxy)phenyl)ethynyl)pyridine S3



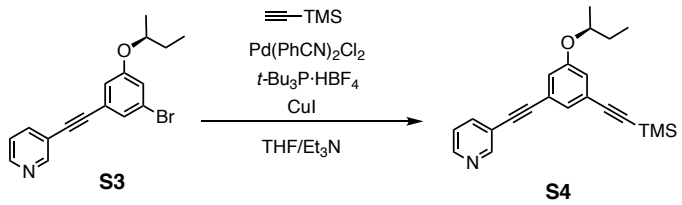
S2 **S3**

A solution of (*S*)-1-bromo-3-(*sec*-butoxy)-5-iodobenzene **S2** (2.25 g, 6.33 mmol) in dehydrated THF (20 mL) and triethylamine (20 mL) was deaerated by the freeze-pump-thaw method. Then bis(triphenylphosphine)palladium(II) dichloride (225 mg, 0.32 mmol), copper(I) iodide (62.5 mg, 0.328 mmol) and 3-(trimethylsilylethynyl)pyridine (1.20 mL, 6.30 mmol) were sequentially added. The mixture was treated with TBAF (ca. 1 M in THF, 7.2 mL) at rt and then stirred at 40 ºC overnight. After evaporation of the reaction mixture, the residue was diluted with dichloromethane and washed with brine. The organic layer was dried over Na_2SO_4 and then concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane, then hexane/ethyl acetate 4/1) to give (*S*)-3-((3-bromo-5-(*sec*-butoxy)phenyl)ethynyl)pyridine **S3** (2.04 g, 98%) as brownish paste.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 8.76 (s, 1H), 8.58 (s, 1H), 7.80 (d, J = 7.9 Hz, 1H), 7.30 (dd, J = 5.0, 7.8 Hz, 1H), 7.25 (s, 1H), 7.06 (s, 1H), 6.98 (s, 1H), 4.33-4.28 (m, 1H), 1.77-1.70 (m, 1H), 1.68-1.61 (m, 1H), 1.31 (d, J = 6.1 Hz, 3H), 0.98 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ 158.81 (C),

152.32 (CH), 148.88 (CH), 138.52 (CH), 126.52 (CH), 124.85 (C), 123.09 (CH), 122.64 (C), 120.25 (CH), 120.01 (C), 117.46 (CH), 91.16 (C), 86.69 (C), 75.79 (CH), 29.07 (CH_2), 19.10 (CH_3), 9.70 (CH_3); HR-ESI-TOF-MS: *m*/*z* calcd. for $C_{17}H_{16}BrNO$: 330.0488 ($[M+H]^+$); found: 330.0488.

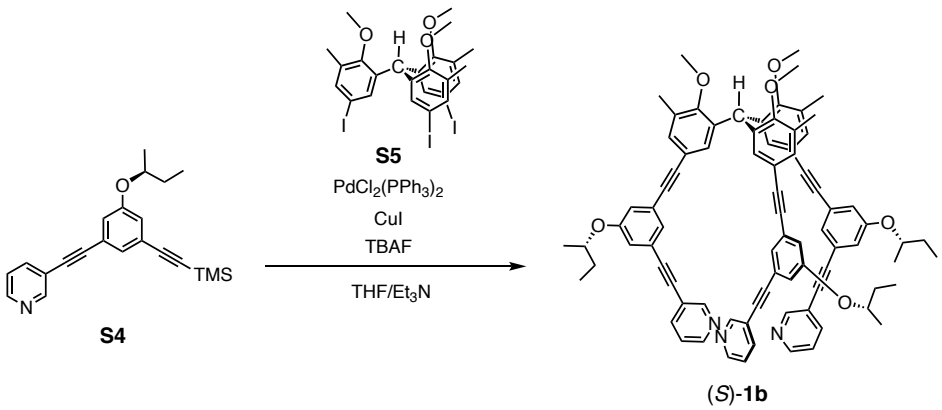
Synthesis of (*S*)-3-((3-((trimethylsilyl)ethynyl)-5-(*sec*-butoxy)phenyl)ethynyl)pyridine S4



A solution of (*S*)-3-((3-bromo-5-(*sec*-butoxy)phenyl)ethynyl)pyridine **S3** (1.89 g, 5.72 mmol) in dehydrated THF (20 mL) and triethylamine (20 mL) was deaerated by the freeze-pump-thaw method. Then bis(benzonitrile)palladium(II) dichloride (115 mg, 0.300 mmol), copper(I) iodide (55.9 mg, 0.294 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (168 mg, 0.579 mmol) and trimethylsilylacetylene (2.4 mL, 17 mmol) were sequentially added and the mixture was stirred at 50 ºC overnight. The reaction mixture was then concentrated under reduced pressure. After dilution with water, the mixture was extracted with ethyl acetate and washed with brine. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane, hexane/ethyl acetate 4/1) to afford protected acetylene **S4** (2.14 g, quant.) as brownish paste.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 8.75 (s, 1H), 8.56 (s, 1H), 7.79 (d, *J* = 7.9 Hz, 1H), 7.29 (dd, *J* = 4.9, 7.8 Hz, 1H), 7.24 (m, 1H), 7.02-7.01 (m, 1H), 6.99-6.98 (m, 1H), 4.34-4.28 (m, 1H), 1.78-1.69 (m, 1H), 1.67-1.60 (m, 1H), 1.30 (d, *J* = 6.1 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.25 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ 158.09 (C), 152.44 (CH), 148.84 (CH), 138.60 (CH), 127.73 (CH), 124.65 (C), 123.76 (C), 123.23 (CH), 120.42 (C), 120.00 (CH), 119.63 (CH), 104.15 (C), 94.95 (C), 91.99 (C), 86.19 (C), 75.71 (CH), 29.28 (CH_2), 19.32 (CH_3), 9.86 (CH_3), 0.04 (CH_3); HR-ESI-TOF-MS: *m*/*z* calcd. for $C_{22}H_{25}NOSi$: 348.1778 ($[M+H]^+$); found: 348.1774.

Synthesis of ligand (*S*)-1b



A solution of triiodide **S5** (993 mg, 1.29 mmol) and protected acetylene **S4** (2.07 g, 5.95 mmol) in dehydrated THF (20 mL) and triethylamine (20 mL) was deaerated by the freeze-pump-thaw method, and

bis(triphenylphosphine)palladium(II) dichloride (101 mg, 0.144 mmol), copper(I) iodide (40.2 mg, 0.211 mmol) and TBAF (ca. 1 M in THF, 1.7 mL) were sequentially added. The mixture was stirred at room temperature for 30 min and then stirred furthermore at 70 ºC overnight. After concentration under reduced pressure, the mixture was extracted with ethyl acetate. The organic layer was washed with brine. Then the solution was dried over Na_2SO_4 and concentrated by evaporation *in vacuo*. The crude product was purified by silica gel column chromatography (chloroform, chloroform/methanol 98/2, then chloroform/methanol 95/5) and filtering out the precipitate in Et_2O to give ligand (*S*)-**1b** (1.21 g, 78 %) as a yellowish solid.

M.p. 208-210 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 8.72 (d, *J* = 1.3 Hz, 3H), 8.52 (dd, *J* = 4.9, 1.6 Hz, 3H), 7.75 (dt, *J* = 7.9, 1.9 Hz, 6H), 7.32 (m, 3H), 7.26-7.23 (m, 6H), 7.02 (s, 3H), 6.99 (s, 3H), 6.94 (s, 3H), 6.54 (s, 1H), 4.33-4.27 (m, 3H), 3.59 (s, 9H), 2.32 (s, 9H), 1.74-1.66 (m, 3H), 1.63-1.59 (m, 3H), 1.26 (d, *J* = 6.0 Hz, 9H), 0.93 (t, *J* = 7.4 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ 158.02 (C), 157.03 (C), 152.26 (CH), 148.64 (CH), 138.47 (CH), 136.90 (CH), 133.93 (CH), 131.65 (C), 131.09 (C), 127.06 (CH), 124.69 (C), 123.66 (C), 123.02 (CH), 120.25 (C), 119.37 (CH), 119.22 (CH), 118.02 (C), 91.94 (C), 90.05 (C), 87.81 (C), 86.01 (C), 75.54 (CH), 60.15 (CH_3), 37.55 (CH), 29.11 (CH_3), 19.17 (CH_2), 16.37 (CH_3), 9.70 (CH_3); HR-ESI-TOF-MS: *m*/*z* calcd. for $C_{82}H_{73}N_3O_6$: 1196.5572 ($[M+H]^+$); found: 1196.5577.

1.3 Supplementary synthesis of ligand (*R*)-1b

Synthesis of **(*R*)-1d** was performed as similar to **(*S*)-1b** above. **(*R*)-1b** appears only in Figures S10 and S14.

(*R*)-1,3-dibromo-5-(*sec*-butoxy)benzene S6

92% yield (colorless oil); ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 7.21 (s, 1H), 6.97 (d, *J* = 1.4 Hz, 2H), 4.28-4.22 (m, 1H), 1.76-1.67 (m, 1H), 1.66-1.57 (m, 1H), 1.28 (d, *J* = 6.1 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ 159.56 (C), 126.04 (C), 123.09 (CH), 118.05 (CH), 75.95 (CH), 29.01 (CH_2), 19.01 (CH_3), 9.66 (CH_3).

(*R*)-1-bromo-3-(*sec*-butoxy)-5-iodobenzene S7

94% yield (colorless oil); ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 7.40 (s, 1H), 7.16 (s, 1H), 6.99 (s, 6H), 4.27-4.21 (m, 1H), 1.75-1.67 (m, 1H), 1.65-1.57 (m, 1H), 1.27 (d, *J* = 6.1 Hz, 3H), 0.96 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ 159.35 (C), 131.66 (CH), 123.96 (CH), 123.11 (C), 118.72 (CH), 94.21 (C), 75.88 (CH), 29.02 (CH_2), 19.01 (CH_3), 9.65 (CH_3).

(*R*)-3-((3-bromo-5-(*sec*-butoxy)phenyl)ethynyl)pyridine S8

99% yield (orange oil); ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 8.76 (s, 1H), 8.57 (d, *J* = 4.2 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.30 (dd, *J* = 5.0, 7.8 Hz, 1H), 7.25 (s, 1H), 7.06 (t, *J* = 1.9 Hz, 1H), 6.98 (s, 1H), 4.33-4.27 (m, 1H), 1.79-1.70 (m, 1H), 1.68-1.60 (m, 1H), 1.31 (d, *J* = 6.1 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ 158.82 (C), 152.32 (CH), 148.88 (CH), 138.52 (CH), 126.53 (CH), 124.86 (C), 123.08 (CH), 122.64 (C), 120.26 (CH), 120.01 (C), 117.47 (CH), 91.15 (C), 86.70 (C), 75.81 (CH), 29.08 (CH_2), 19.10 (CH_3), 9.70 (CH_3); HR-ESI-TOF-MS: *m*/*z* calcd for $C_{17}H_{16}BrNO$: 330.0488 ($[M+H]^+$); found: 330.0483.

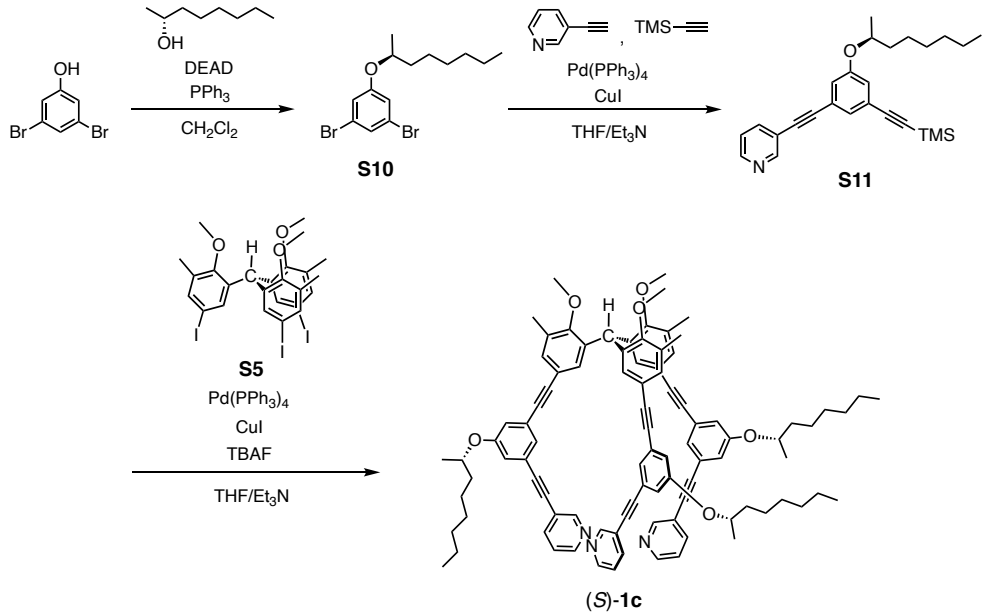
(*R*)-3-((3-((trimethylsilyl)ethynyl)-5-(*sec*-butoxy)phenyl)ethynyl)pyridine S9

Quant. (brown oil); ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 8.75 (d, *J* = 1.0 Hz, 1H), 8.55 (dd, *J* = 5.0, 1.5 Hz, 1H), 7.79 (dt, *J* = 6.0, 1.8 Hz, 1H), 7.29 (dd, *J* = 4.9, 7.8 Hz, 1H), 7.24 (m, 1H), 7.02-7.01 (m, 1H), 6.99-6.98 (m, 1H), 4.34-4.28 (m, 1H), 1.78-1.69 (m, 1H), 1.66-1.59 (m, 1H), 1.30 (d, *J* = 6.1 Hz, 3H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.25 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ 158.08 (C), 152.42 (CH), 148.82 (CH), 138.59 (CH), 127.73 (CH), 124.64 (C), 123.75 (C), 123.21 (CH), 120.40 (C), 119.99 (CH), 119.63 (CH), 104.14 (C), 94.94 (C), 91.99 (C), 86.19 (C), 75.70 (CH), 29.27 (CH_2), 19.31 (CH_3), 9.86 (CH_3), 0.04 (CH_3); HR-ESI-TOF-MS: *m*/*z* calcd for $C_{22}H_{25}NOSi$: 348.1778 ($[M+H]^+$); found: 348.1771.

Ligand (*R*)-1b

23% yield (a yellowish solid); m.p. 208-210 °C; ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 8.72 (s, 3H), 8.52 (d, *J* = 4.0 Hz, 3H), 7.75 (d, *J* = 7.5 Hz, 6H), 7.32 (s, 3H), 7.26-7.23 (m, 6H), 7.02 (s, 3H), 6.99 (s, 3H), 6.94 (s, 3H), 6.54 (s, 1H), 4.33-4.27 (m, 3H), 3.59 (s, 9H), 2.32 (s, 9H), 1.75-1.66 (m, 3H), 1.63-1.57 (m, 3H), 1.26 (d, *J* = 6.0 Hz, 9H), 0.93 (t, *J* = 7.4 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ 158.02 (C), 157.03 (C), 152.27 (CH), 148.64 (CH), 138.46 (CH), 136.90 (CH), 133.92 (CH), 131.65 (C), 131.09 (C), 127.06 (CH), 124.68 (C), 123.66 (C), 123.02 (CH), 120.25 (CH), 119.37 (CH), 119.22 (CH), 118.02 (C), 91.94 (C), 90.05 (C), 87.81 (C), 86.02 (C), 75.54 (CH), 60.15 (CH_3), 37.55 (CH), 29.11 (CH_3), 19.17 (CH_2), 16.37 (CH_3), 9.70 (CH_3); HR-ESI-TOF-MS: *m*/*z* calcd for $C_{82}H_{73}N_3O_6$: 1196.5572 ($[M+H]^+$); found: 1196.5538.

1.4 Synthesis of ligand (*S*)-1c



Synthesis of (*S*)-1-(sec-octoxy)-3,5-dibromobenzene S10

A solution of 3,5-dibromophenol (2.00 g, 7.94 mmol), (*R*)-2-octanol (1.15 mL, 7.22 mmol) and triphenylphosphine (2.11 g, 8.04 mmol) in CH_2Cl_2 (30 mL) was cooled to 0 °C. To the solution was slowly added DEAD (3.77 mL, 8.30 mmol). After the mixture was stirred at room temperature for 2 h, temperature was elevated to 40 °C and furthermore stirred overnight. After removal of the solvent under reduced pressure,

hexane was added and the precipitation was filtered out. After evaporation, the residue was extracted with Et_2O and washed with saturated Na_2CO_3 aq. and brine. The organic layer was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (hexane) to give **S10** (2.18 g, 76%) as colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 7.13 (s, 1H), 6.88 (s, 2H), 4.25-4.19 (m, 1H), 1.65-1.58 (m, 1H), 1.51-1.44 (m, 1H), 1.36-1.30 (m, 1H), 1.27-1.19 (m, 10H), 0.81 (t, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, 287 K): δ 159.51 (C), 125.97 (CH), 123.12 (C), 117.93 (CH), 74.74 (CH), 36.26 (C), 31.80 (C), 29.24 (C), 25.42 (C), 22.65 (C), 19.51 (CH_3), 14.17 (CH_3).

Synthesis of (*S*)-3-((3-(octan-2-yloxy)-5-((trimethylsilyl)ethynyl)phenyl)ethynyl)pyridine S11

A solution of (*S*)-1-(sec-octoxy)-3,5-dibromobenzene **S10** (1.20 g, 3.30 mmol) in dehydrated THF (30 mL) and triethylamine (30 mL) was deaerated by the freeze-pump-thaw method. Then tetrakis(triphenylphosphine)palladium(0) (359 mg, 0.311 mmol), copper(I) iodide (90.3 mg, 0.474 mmol), 3-ethynylpyridine (320 mg, 3.10 mmol) and trimethylsilylacetylene (0.84 mL, 3.44 mmol) were sequentially added and the mixture was stirred at 50 ºC overnight. The reaction mixture was then concentrated under reduced pressure. After dilution with water, the mixture was extracted with ethyl acetate and washed with brine. The organic layer was dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was roughly separated by silica gel column chromatography (hexane then hexane/ethyl acetate 9/1) to afford protected acetylene **S11** (316 mg, 25 % if pure) as brown paste. After dried *in vacuo*, the residue was used for the next step without further purification.

HR-ESI-TOF-MS: *m*/*z* calcd. for $C_{26}H_{34}NOSi$: 404.2410 ($[M+H]^+$); found: 404.2397.

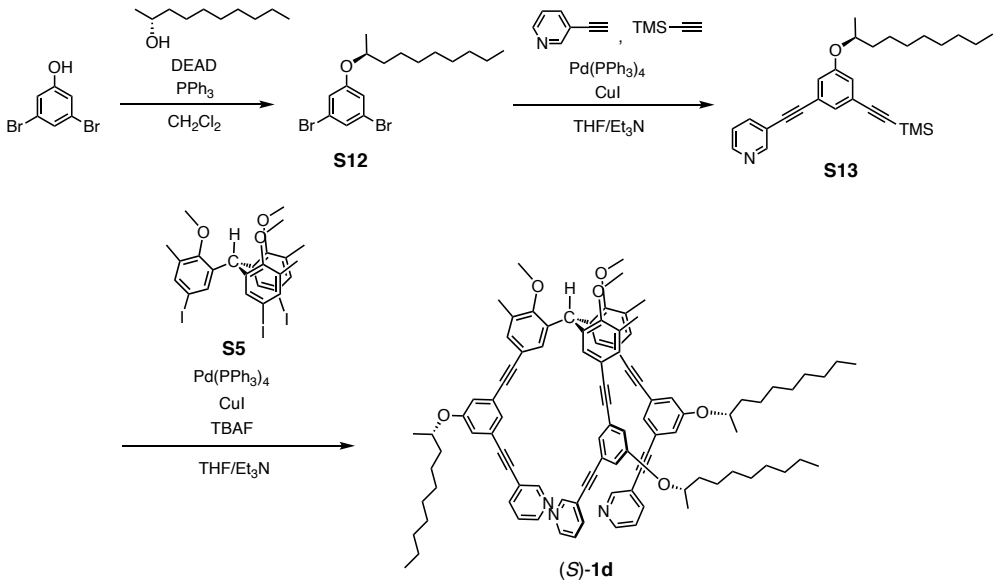
Synthesis of ligand (*S*)-1c

A solution of triiodide **S5** (124 mg, 0.164 mmol) and protected acetylene **S11** (300 mg, 0.743 mmol) in dehydrated THF (20 mL) and triethylamine (20 mL) was deaerated by the freeze-pump-thaw method, and tetrakis(triphenylphosphine)palladium(0) (35 mg, 0.030 mmol), copper(I) iodide (7.0 mg, 0.036 mmol) and tetrabutylammonium fluoride (ca. 1 M in THF, 1.0 mL) were sequentially added. The mixture was stirred at room temperature for 30 min and then furthermore stirred at 70 ºC overnight. After concentration under reduced pressure, the mixture was diluted with ethyl acetate. The organic layer was washed with brine. Then the solution was dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (chloroform, then chloroform/methanol 97/3) and removing precipitate in Et_2O to give ligand **(*S*)-1c** (114 mg, 52 %) as a brown solid.

M.p. 74.8-76.6 ºC; ^{1}H NMR (500 MHz, $CDCl_3$, 287 K): δ 8.72 (s, 3H), 8.54 (3H), 7.76 (d, J = 7.85 Hz, 3H), 7.33 (s, 3H), 7.27-7.25 (m, 6H, overlapped with the solvent peak), 7.01 (s, 3H), 6.98 (s, 3H), 6.93 (s, 3H), 6.53 (s, 1H), 4.37-4.33 (m, 3H), 3.60 (s, 9H), 2.32 (s, 9H), 1.71-1.65 (3H), 1.56-1.51 (m, 3H), 1.41-1.38 (m, 3H), 1.32-1.25 (30H), 0.85 (t, J = 6.4 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ 157.97 (C), 156.97 (C), 152.23 (CH), 148.70 (CH), 138.54 (CH), 136.87 (C), 133.97 (CH), 131.69 (C), 131.05 (CH), 127.01 (CH), 124.65 (C), 123.62 (C), 123.12 (CH), 120.26 (C), 119.29 (CH), 119.07 (CH), 118.01 (C), 91.97 (C),

90.03 (C), 87.81 (C), 85.99 (C), 74.32 (CH), 60.19 (CH), 37.57 (CH), 36.41 (CH_2), 31.78 (CH_2), 29.24 (CH_2), 25.43 (CH_2), 22.63 (CH_2), 19.65 (CH_3), 16.42 (CH_3), 14.15 (CH_3); HR-ESI-TOF-MS: *m*/*z* calcd. for $C_{94}H_{98}N_3O_6$: 1365.7489 ($[M+H]^+$); found: 1365.7460.

1.5 Synthesis of ligand (*S*)-1d



Synthesis of **(*S*)-1b** was performed as similar to **(*S*)-1c** above.

(*S*)-1,3-dibromo-5-(decan-2-yloxy)benzene S12

^{1}H NMR (500 MHz, $CDCl_3$, 287 K): δ 7.20 (m, 1H), 6.96 (d, *J* = 2.0 Hz, 2H), 4.32-4.26 (m, 1H), 1.73-1.66 (m, 1H), 1.57-1.51 (m, 1H), 1.44-1.34 (m, 1H), 1.34-1.27 (14H), 0.88 (t, *J* = 6.9 Hz, 3H) ; ^{13}C NMR (126 MHz, $CDCl_3$, 287 K): δ 159.51 (C), 125.97 (CH), 123.12 (C), 117.93 (CH), 74.74 (CH). 36.26 (CH_2), 31.92 (CH_2), 29.57 (CH_2), 29.56 (CH_2), 29.30 (CH_2), 25.45 (CH_2), 22.74 (CH_2), 19.51 (CH_3), 14.21 (CH_3).

(*S*)-3-((3-(decan-2-yloxy)-5-((trimethylsilyl)ethynyl)phenyl)ethynyl)pyridine S13

^{1}H NMR (500 MHz, $CDCl_3$, 287 K): δ 8.75 (s, 1H), 8.56 (d, *J* = 4.0 Hz, 1H), 7.80-7.78 (m, 1H), 7.30 (dd, *J* = 4.9, 7.8 Hz, 1H), 7.24 (s, 1H), 7.01 (d, *J* = 1.0 Hz, 1H), 6.98 (d, *J* = 1.0 Hz, 1H), 4.39-4.33 (m, 1H), 1.71-1.43 (m, 3H), 1.37-1.26 (14H), 0.88 (t, *J* = 1.4 Hz, 3H), 0.25 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$, 287 K): δ 157.90 (C), 152.30 (CH), 148.74 (CH), 138.53 (CH), 127.55 (CH), 124.45 (C), 123.59 (C), 123.12 (CH), 120.22 (C), 119.74 (CH), 119.40 (CH), 103.99 (C), 94.81 (C), 91.85 (C), 86.04 (C), 74.35 (CH), 36.42 (CH_2), 31.91 (CH_2), 29.58 (CH_2), 29.30 (CH_2), 25.49 (CH_2), 22.72 (CH_2), 19.67 (CH_3), 14.20 (CH_3), −0.07 (CH_3); HR-ESI-TOF-MS: *m*/*z* calcd. for $C_{28}H_{38}N_3O_6$: 432.2723 ($[M+H]^+$); found: 432.2739.

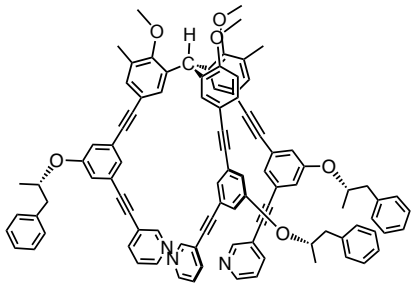
Ligand (*S*)-1b

M.p. 59.2-61.4 ºC; ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ 8.73 (s, 3H), 8.54 (3H), 7.76 (d, *J* = 7.6 Hz, 3H), 7.33 (s, 3H), 7.27 (m, 6H, overlapped with the residual solvent peak), 7.02 (s, 3H), 6.99 (s, 3H), 6.93 (s, 3H), 6.53 (s, 1H), 4.37-4.34 (m, 3H), 3.60 (s, 9H), 2.33 (s, 9H), 1.68-1.63 (brm, 3H, overlapped with H_2O peak),

1.56-1.50 (brm, 3H), 1.41-1.38 (brm, 3H), 1.38-1.24 (brm, 42H), 0.85 (t, J = 6.7 Hz, 9H); ^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ 157.97 (C), 156.97 (C), 152.24 (CH), 148.66 (CH), 138.51 (CH), 136.87 (C), 133.97 (CH), 131.69 (C), 131.05 (CH), 127.01 (CH), 124.64 (C), 123.63 (C), 123.10 (CH), 120.26 (C), 119.28 (CH), 119.06 (CH), 118.01 (C), 91.97 (C), 90.03 (C), 87.82 (C), 86.02 (C), 74.32 (CH), 60.19 (CH_3), 37.57 (CH), 36.42 (CH_2), 31.89 (CH_2), 29.58 (CH_2), 29.55 (CH_2), 29.28 (CH_2), 25.47 (CH_2), 22.71 (CH_2), 19.65 (CH_3), 16.43 (CH_3), 14.19 (CH_3). HR-ESI-TOF-MS: *m*/*z* calcd. for $C_{85}H_{80}N_3O_6$: 1449.8428 ($[M+H]^+$); found: 1449.8361.

1.5 Supplementary synthesis of ligand (*S*)-1e

Synthesis of **(*S*)-1e** was performed as similar to **(*S*)-1b-d** above.



(*S*)-1e: M.p.97.0-98.3 ºC; ^{1}H NMR (500 MHz, $CDCl_3$, 287 K): δ 8.71 (d, J =1.0 Hz, 3H), 8.52 (dd, J = 4.8 Hz, 1.3 Hz, 3H), 7.74 (dd, J = 8.0, 1.5 Hz, 3H), 7.33 (d, J =1.0 Hz, 3H), 7.27-7.26 (3H, overlapped with the residual solvent peak), 7.25-7.15 (18H), 7.00 (s, 3H), 6.97 (s, 3H), 6.93 (s, 3H), 6.53 (s, 1H), 4.59-4.56 (m, 3H), 3.60 (s, 9H), 3.02 (dd, J = 14, 6.3 Hz, 3H), 2.81 (dd, J =14, 6.3 Hz, 3H), 2.33 (s, 9H), 1.27-1.26 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$, 300 K): δ 157.59 (C), 156.99 (C), 152.25 (CH), 148.70 (CH), 138.53 (CH), 137.82 (C), 136.88 (C), 133.99 (CH), 131.72 (C), 131.06 (CH), 129.52 (CH), 128.37 (CH), 127.24 (CH), 126.48 (C), 124.70 (C), 123.69 (C), 123.09 (CH), 120.18 (C), 119.38 (CH), 119.06 (CH), 117.97 (C), 91.85 (C), 90.15(C) , 87.75 (C), 86.14 (C), 75.00 (CH), 60.20 (CH_3), 42.56 (CH_2), 37.56 (CH), 19.30 (CH_3), 16.43 (CH_3); HR-ESI-TOF-MS: *m*/*z* calcd. for $C_{97}H_{80}N_3O_6$: 1383.6081 ($[M+H]^+$); found: 1383.6049.

1.6 Representative procedures for the self-assembly of $(M_3L_2)_n$ polyhedra

Self-assembly of $(M_3L_2)_2$ assembly 2 (M = Cu^I)

A solution of ligand (*S*)-**1b** (2.50 mg, 2.09 μmol) in CD_3NO_2 (418 μL) was mixed with $[Cu(MeCN)_4]BF_4$ (1.02 mg, 3.25 μmol, in CD_3NO_2 (418 μL)) in a glass vial, and the mixture was stirred at 50 ºC for 1 h. Convergence to **2b** (= $[(Cu_3(\mathbf{1b})_2)_2](BF_4)_6$) was confirmed by ^1H and ^{13}C NMR (Figures S21 and S22) together with ^1H–^1H COSY and ^1H–^{13}C HMQC/HMBC measurements (Figures S23-S26).

A self-assembly experiment with ligand **1e** was conducted in the same procedure, using **1e** (2.24 mg, 1.62 μmol) and $[Cu(MeCN)_4]BF_4$ (0.794 mg, 2.52 μmol) in CD_3NO_2 (650 μL).

Self-assembly of $(M_3L_2)_4$ tetrahedron 3 (M = Cu^I)

A solution of ligand (*S*)-**1b** (4.09 mg, 3.42 μmol) in toluene-d_8 (650 μL, deaerated by bubbling Ar gas for ca. 10 min) was mixed with $[Cu(MeCN)_4]BF_4$ (1.73 mg, 5.50 μmol, in toluene-d_8 (650 μL, deaerated as above)) in a glass vial, and the mixture was stirred at 50 ºC for 30 min. Convergence to **3b** (= $[(Cu_3(\mathbf{1b})_2)_4](BF_4)_{12}$) was confirmed by ^1H and ^{13}C NMR (Figures S27 and S28) together with 2D NMR measurements (Figures S29-S31). Self-assembly experiments in different solvents were conducted in the same procedure, respectively.

Self-assembly of $(M_3L_2)_8$ cube 4 (M = Ag^I)

A solution of dimeric assembly **2b** ((*S*)-**1b** : 3.03 mg, 2.53 μmol) prepared with $AgPF_6$ (1.26 mg, 5.00 μmol) in $CDCl_3$ (1.00 mL)/CD_3OD (31 μL) was treated with $TBANO_3$ (1.15 mg, 3.77 mmol) in a glass vial at rt, and the interconversion into cube **4b** was confirmed by ^1H NMR (Figures S11 and S32) and ^{13}C NMR (Figure S33) after ca. 10 min.

Self-assembly experiments with ligands **1c** and **1d** were also conducted in the same procedure, respectively as follows.

4c: **1c** (2.44 mg, 1.79 μmol), $AgSbF_6$ (1.23 mg, 3.58 μmol), $TBANO_3$ (0.75 mg, 2.46 μmol) in $CDCl_3$ (650 μL)/CD_3OD (40 μL).

4d: **1d** (2.28 mg, 1.57 μmol), $AgSbF_6$ (1.12 mg, 3.25 μmol), $TBANO_3$ (0.48 mg, 1.57 μmol) in $CDCl_3$ (650 μL)/CD_3OD (20 μL).

As previously reported,[S3] in the case of ligand **1a** without any side chain, the addition of 0.5 equiv (*vs* **1a**) of nitrate to **2a** afforded cube **4a**, indicating the anion exchange inside 8 M_3L_2 subunits (binding a nitrate ion respectively) is enough to completion of the interconversion irrespective of 16 residual counter anions. Although in the current study, molar equivalents of nitrate ion (0.5 to 1.5 equiv) required for the completion of the interconversion depended on the ligands with different chiral groups, possibly due to steric effects of the accumulated side chains affecting the relative stability of the cubic framework under thermodynamic conditions.

2. Supplementary figures

Unless otherwise noted, (*S*)-isomers of **1a-e** were used for studies in this section.

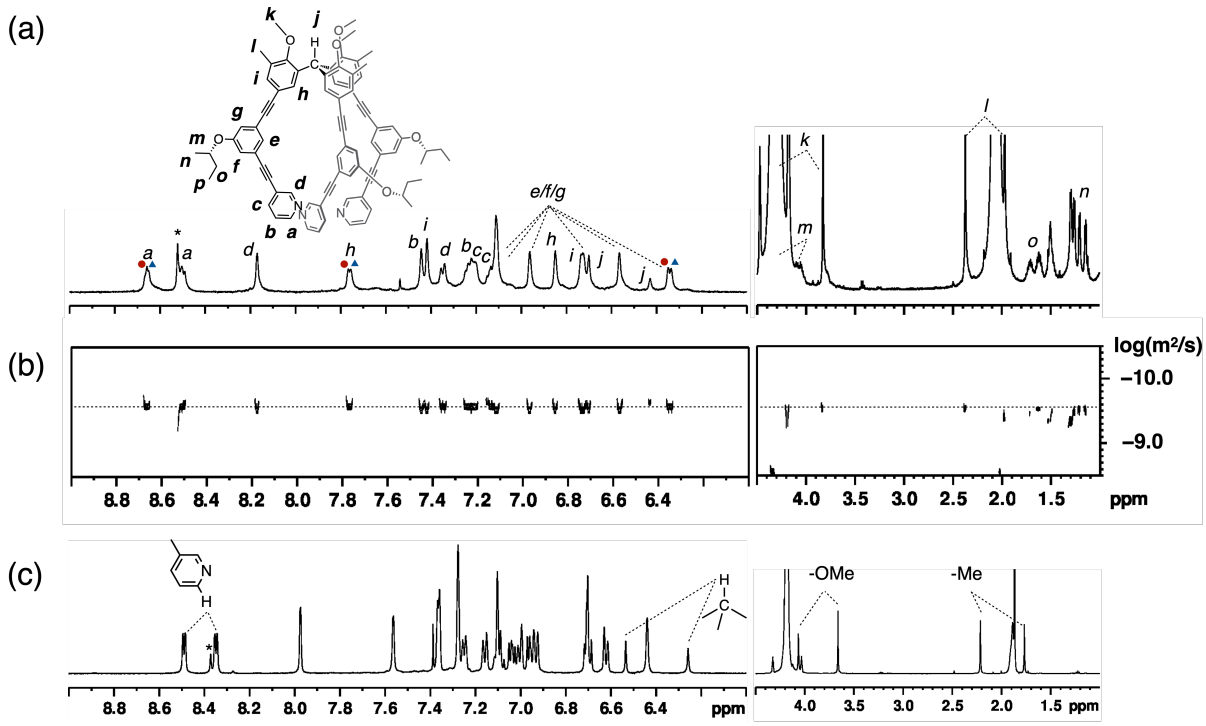


Figure S1. (a) ^{1}H NMR (500 MHz, 300 K) spectrum of the assembly of **1b** with $CuBF_4$ (**2b**, CD_3NO_2). (b) ^{1}H DOSY spectrum of (a). (c) ^{1}H NMR (500 MHz, 300 K) spectra of the dimeric assembly **2a** prepared from **1a** and $CuBF_4$ (in CD_3NO_2) [S1] shown as a reference. *: impurity derived from the solvent. Red circles and blue triangles indicate two diastereomeric assemblies, respectively.

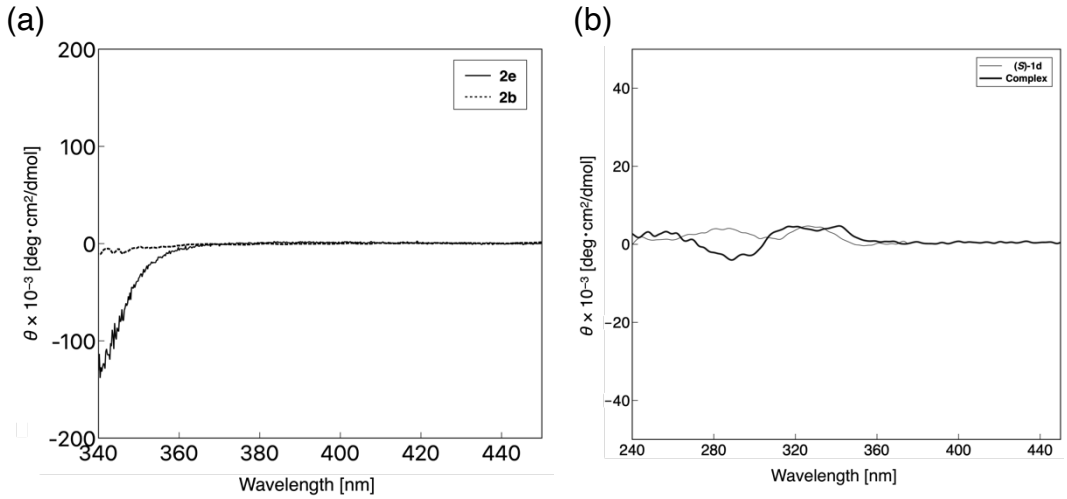


Figure S2. (a) CD spectra of the dimeric assembly **2b** and **2e** (with $CuBF_4$, nitromethane, 293 K). Free ligands **1d** and **1e** were poorly soluble in nitromethane. In nitromethane, spectra could be obtained over 340 nm due to severe interference by the solvent absorption. (b) Supplementary CD spectra of **2b** and ligand (*S*)-**1b** in $CHCl_3$ (293 K) for checking the profile in the range of lower wavelengths. For selective formation of **2** in $CHCl_3$, CuOTf was used in place of $CuBF_4$ to apply the steric effect of encapsulated OTf^- ions suppressing the formation of higher oligomeric cage **3** (ref. S1 and S3).

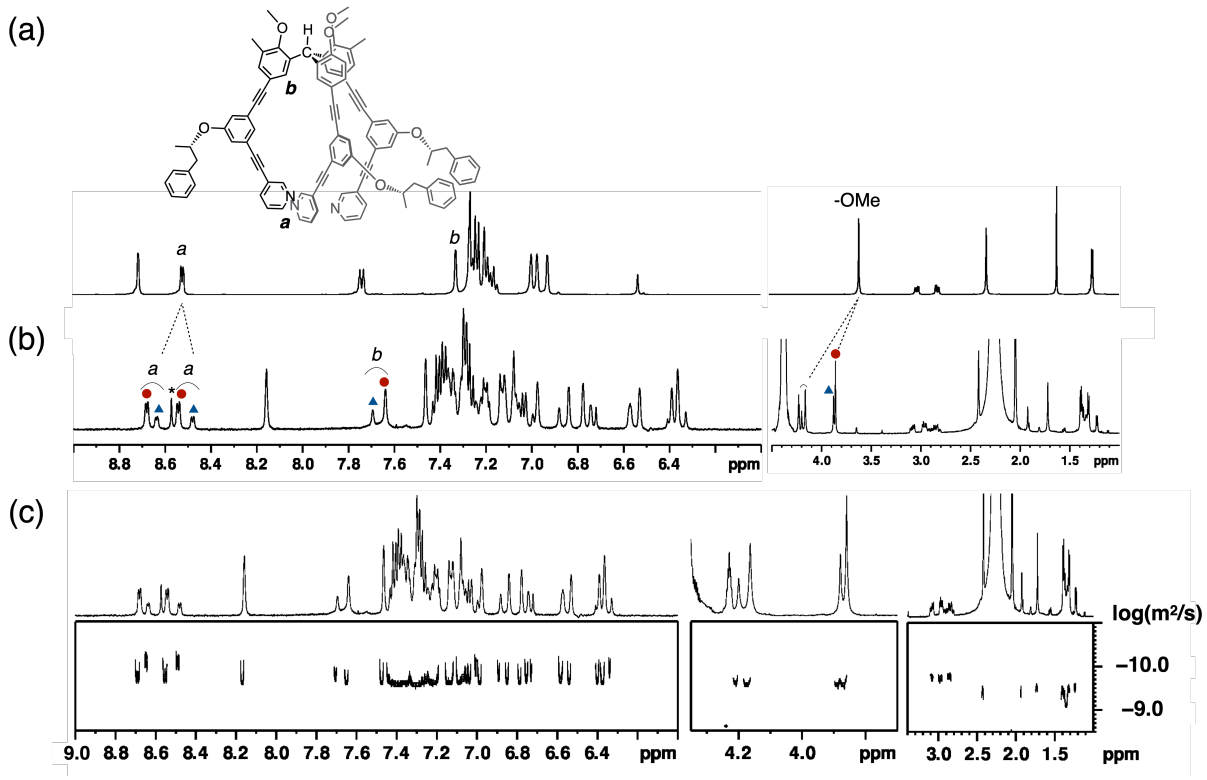


Figure S3. ^1H NMR spectra (500 MHz, 300 K) of (a) ligand **1e** (in $CDCl_3$), (b) the assembly of **1e** with $CuBF_4$ (**2e**, CD_3NO_2), (c) ^1H DOSY NMR spectrum of (b). *: impurity derived from the solvent. Red circles and blue triangles indicate two diastereomeric assemblies, respectively.

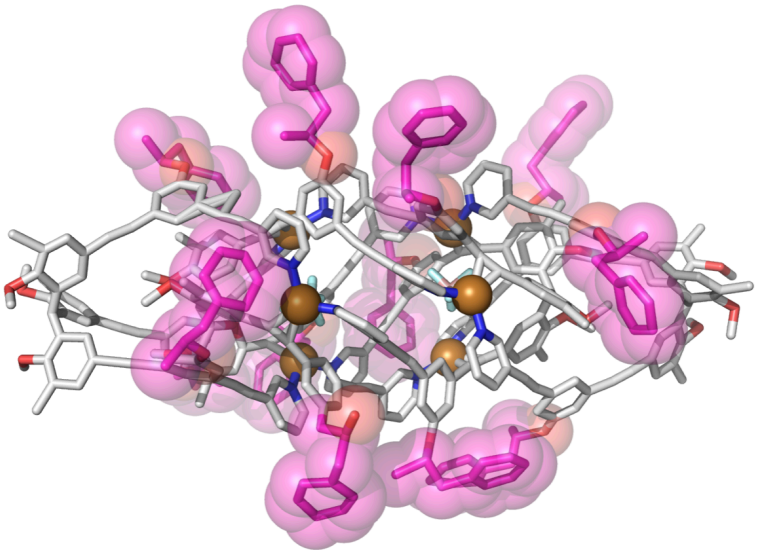


Figure S4. X-ray/MM structure of the assembly **2e** (M = Cu(I)). (*S*)-1-phenyl-2-propanoxy groups are colored magenta.

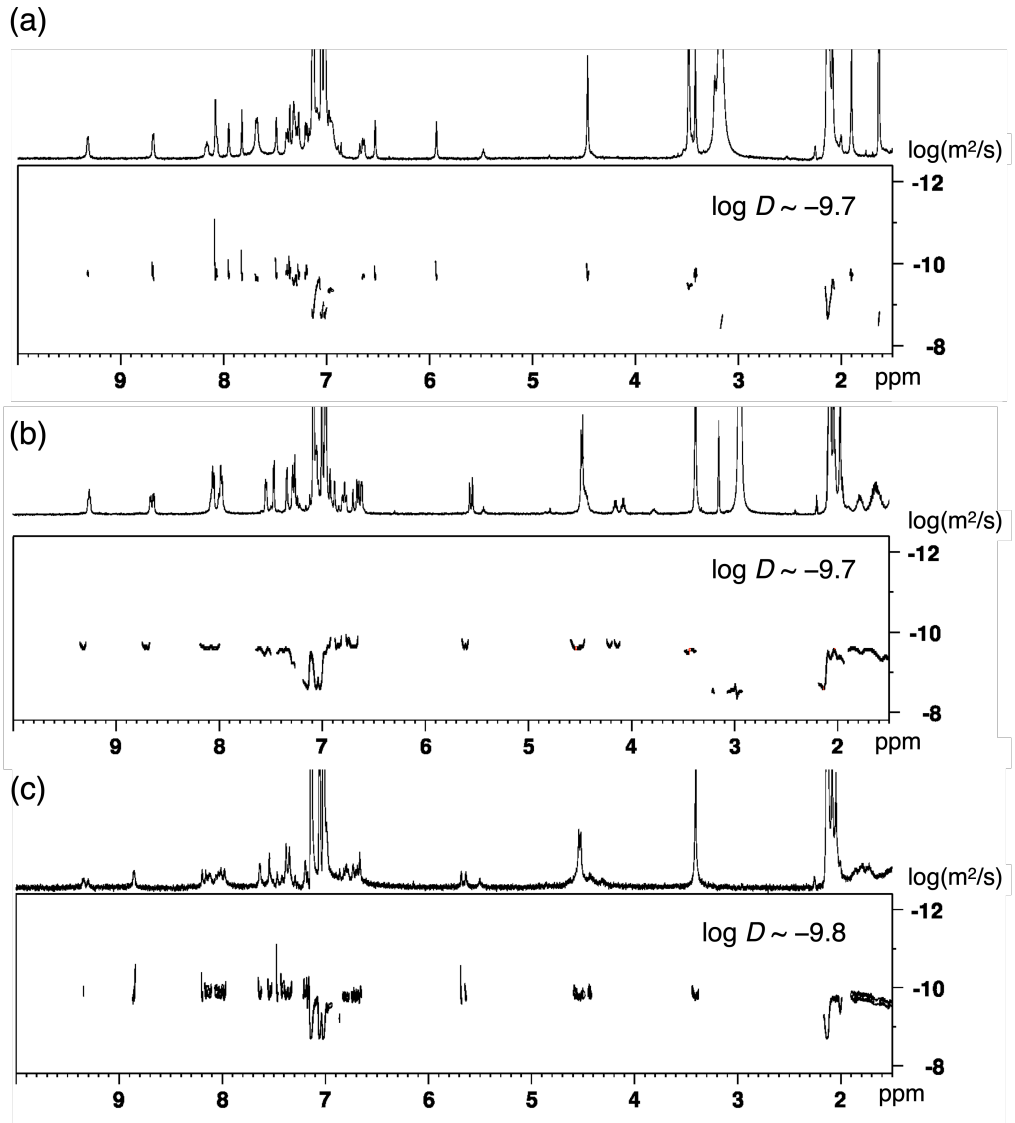


Figure S5. ^{1}H DOSY NMR spectra (500 MHz, 300 K) of (a) the assembly of **1a** with $CuBF_4$ (**3a**, toluene-d_8/MeOD (94/6)), (b) the assembly of **1b** with $CuBF_4$ (**3b**, toluene-d_8/MeOD (94/6)), (c) **3b** (in toluene-d_8).

Figure S5(a) and S5(b) show the comparable diffusion constants between previously reported assembly **3a** and currently studied **3b**. According to the diffusion constant (log D ~ −9.77) in pure toluene-d_8 (viscosity = 0.541 cP in 300 K)[S4] as shown in Figure S5(c), estimated to be 4.7 nm of diameter, which is similar to that of the main framework of assembly **3** determined by X-ray analysis (4.5 nm).[S1] DOSY signals of **3a** in pure toluene-d_8 could not be analyzed well due to relatively poorly soluble state.

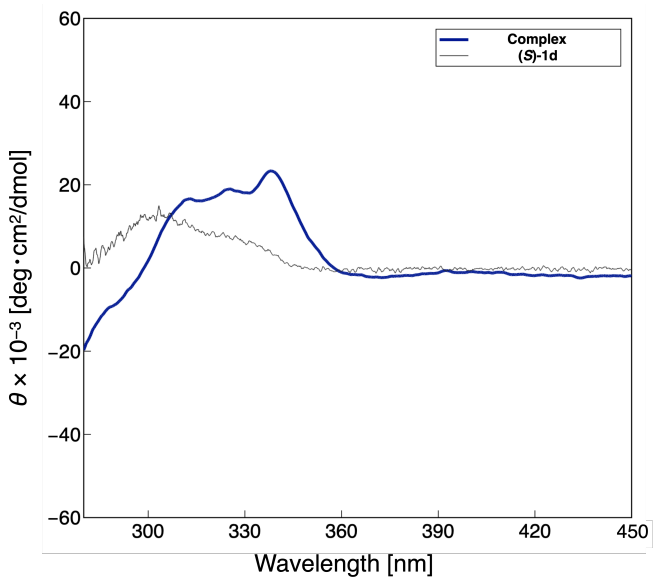


Figure S6. CD spectra of tetrahedron **3b** and ligand **1b** (toluene, 293 K).

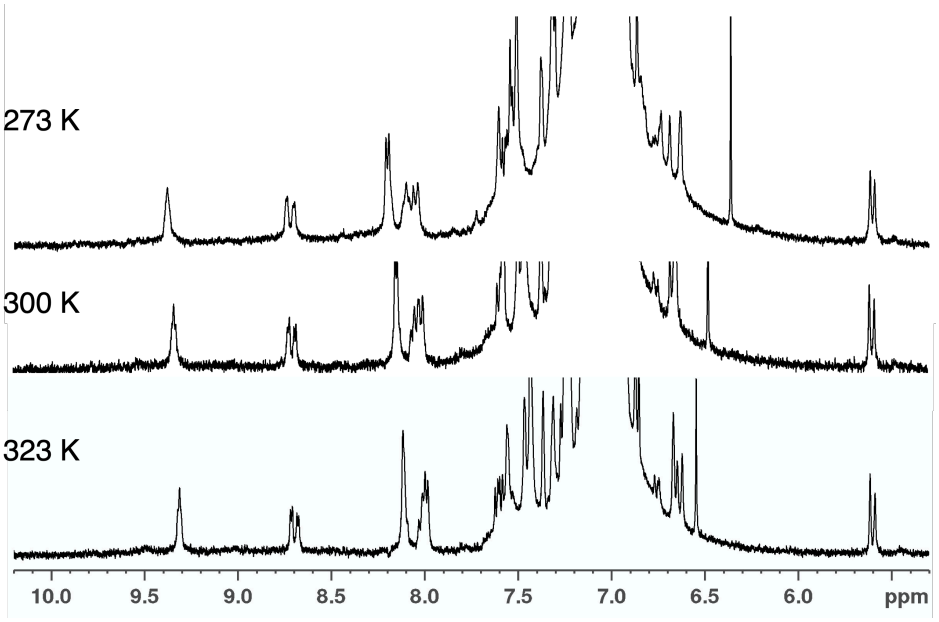


Figure S7. VT-^{1}H NMR spectra (500 MHz, toluene-d_8/MeOD (90/10)) of tetrahedron **3c**.

Moderate diastereomeric ratios in the self-assembly of tetrahedron **3** enabled us to obtain detailed information for the chirality multiplication process. Notably, selectivity is significantly influenced by solvent polarity. Complexation of **1b** and $CuBF_4$ was conducted in toluene-d_8/CD_3OD in varied ratio (v/v 100/0 to 50/50) showed that the diastereoselectivity even inverted (52:48 to 39:61), as confirmed by ^1H NMR (Figure S8a) and CD spectral changes (b). A plausible explanation of the solvent effects is that alkyl moieties of the side chains are relatively hydrophobic to direct outward in hydrophobic solvent (*i.e.* toluene-d_8), while tilting toward the cage framework in polar environments upon addition of methanol. This difference possibly causes the degree of steric congestion effects among accumulated side chains.[S5] Solvent effects in other solvents were also observed (Figure S9). In addition, the self-assembly of **3b** with (*R*)-isomer ligand ((*R*)-**1b**) was also confirmed by CD measurements (Figure S10).

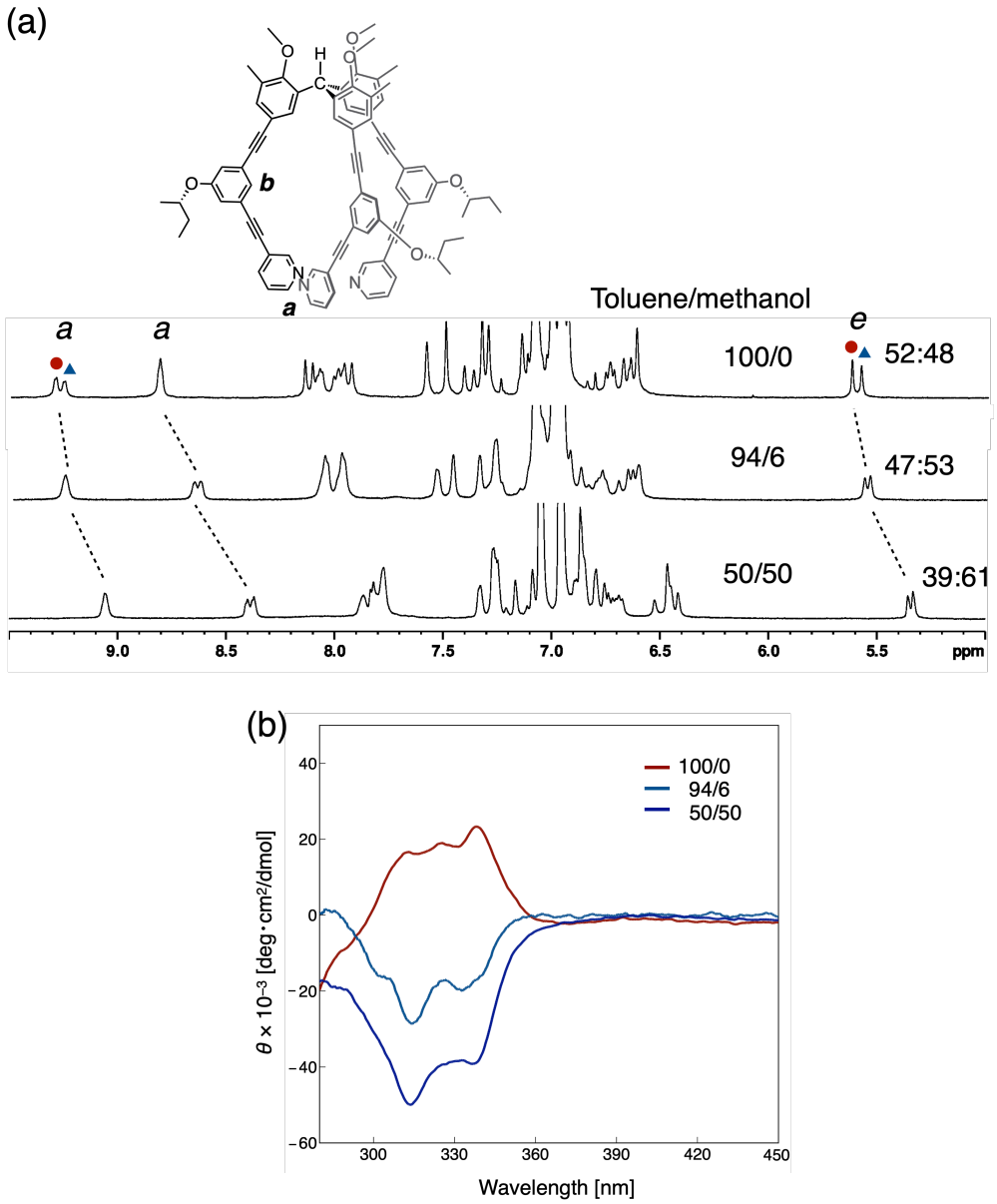


Figure S8. (a) ^1H NMR spectra (500 MHz, 300 K) of tetrahedron **3b** (ligand: **1b**) formed in toluene-d_8/CD_3OD with varied ratios. (b) CD spectra (293 k) of tetrahedron **3b** self-assembled in varied ratios of toluene/MeOH.

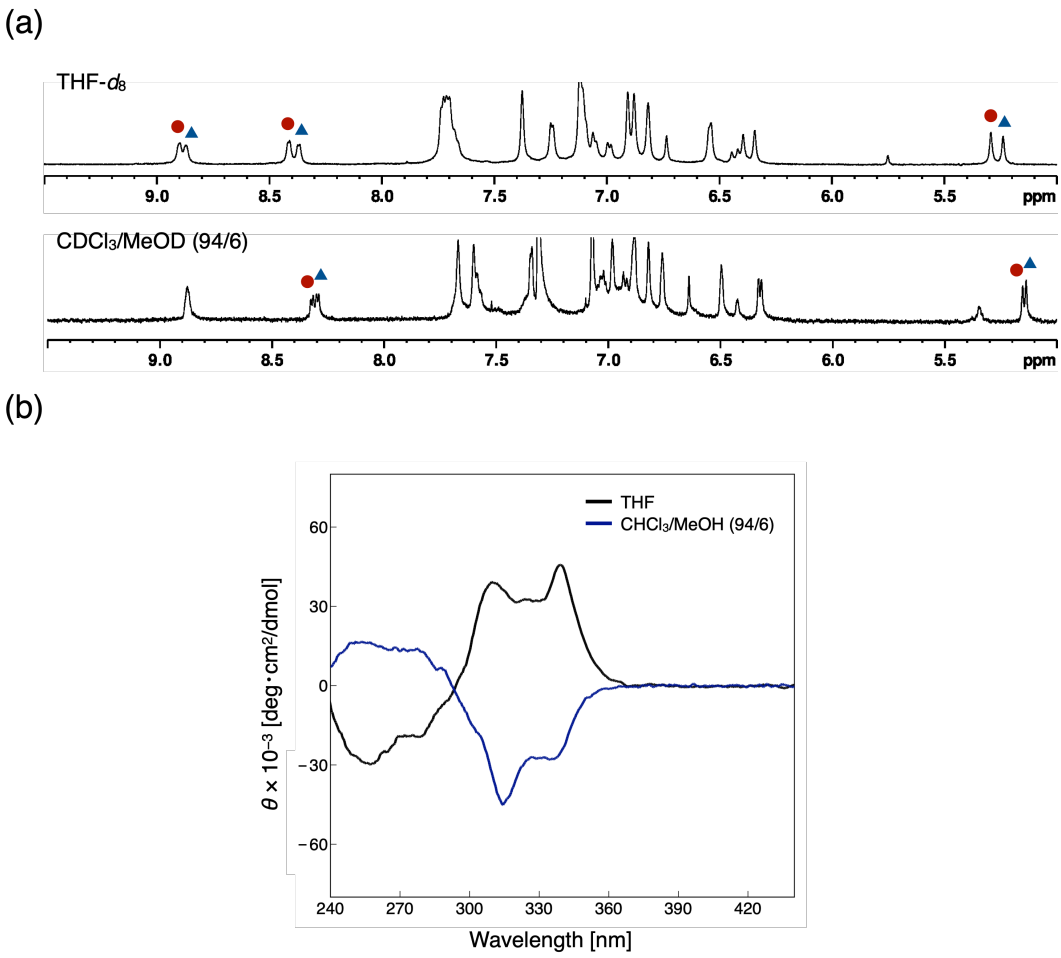


Figure S9. (a) ^{1}H NMR spectra (500 MHz, 300 K) of tetrahedron **3b** in THF-d_8 or $CDCl_3$/MeOD (94/6). (b) CD spectra (293 K) of **3b** in THF or $CHCl_3$/MeOH (94/6).

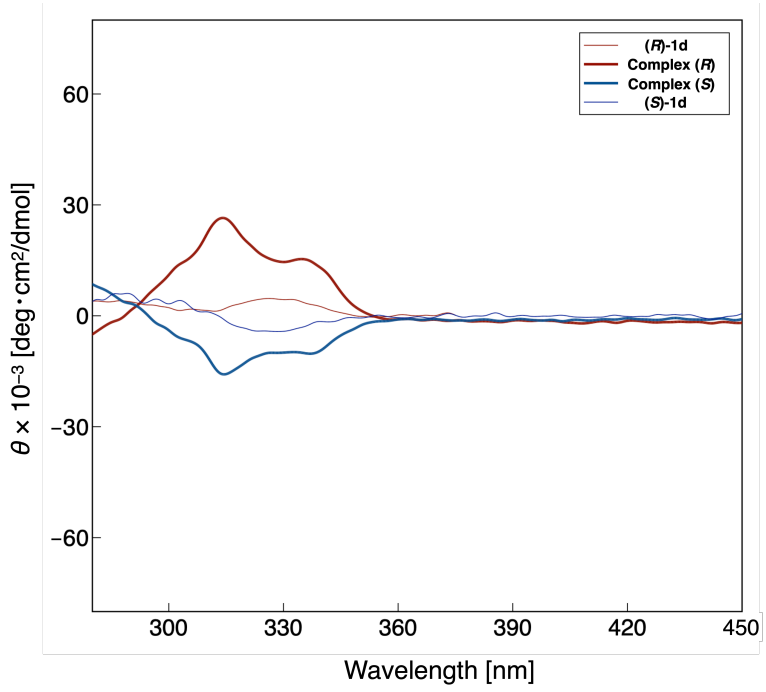


Figure S10. CD spectra of $[(Cu_3((R \text{ or } S)\text{-}\mathbf{1b})_2)_4](BF_4)_{12}$ (= **3b**) and ligand (*R* or *S*)-**1b** ($CHCl_3$, 293 K).

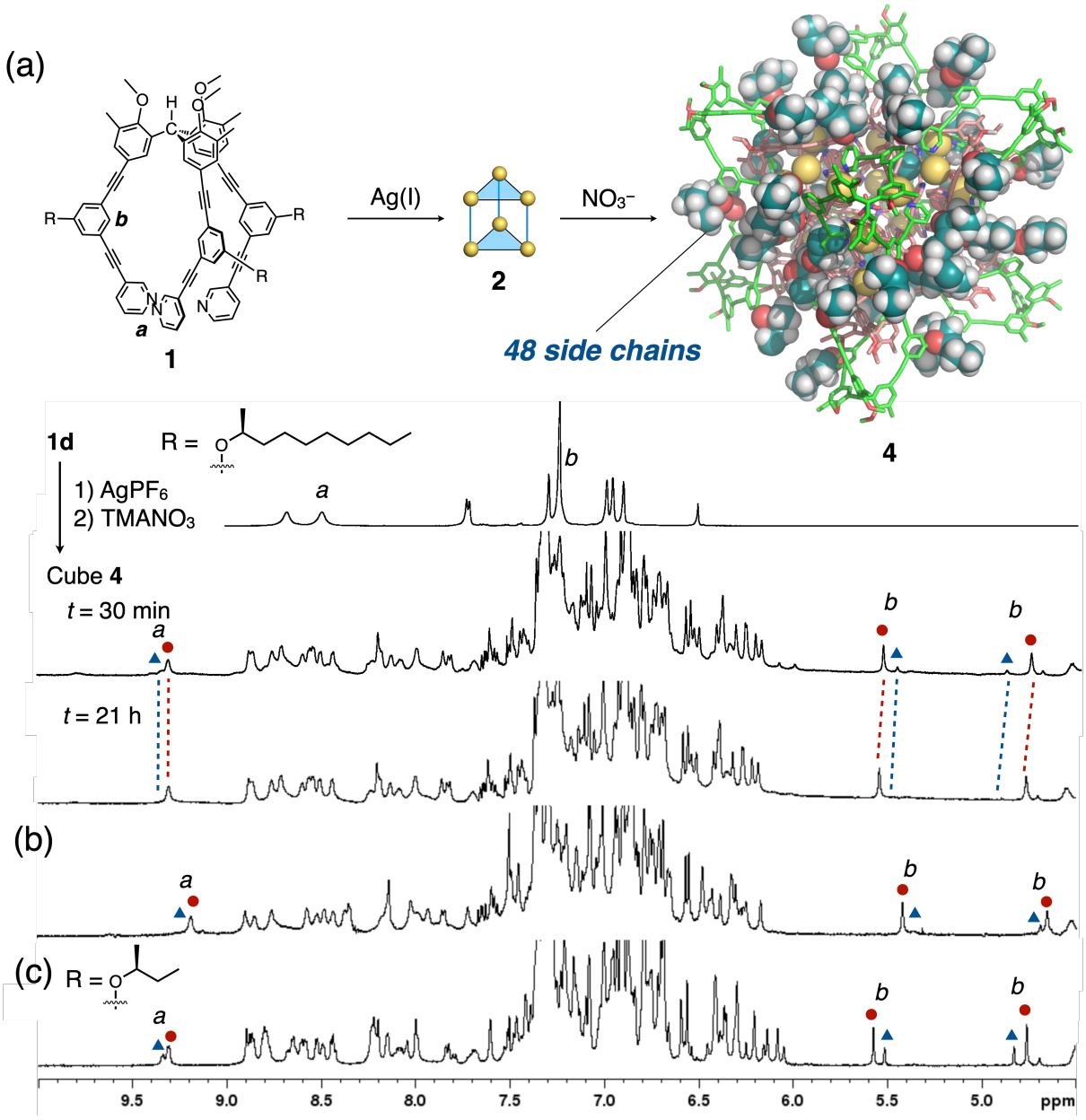


Figure S11. Self-assembly of cubic assembly **4** with ligands equipped with chiral side chains. (a) ^{1}H NMR spectra (500 MHz, 287 K, $CDCl_3/CD_3OD$ (94/6)) of ligand **1d** and cube **4d** showing time-dependent redistribution of the diastereomers, (b) cube **4d** with ligand **1d** in $CDCl_3/CD_3OD$ (97/3), and (c) cube **4b** with ligand **1b** in $CDCl_3/CD_3OD$ (97/3).

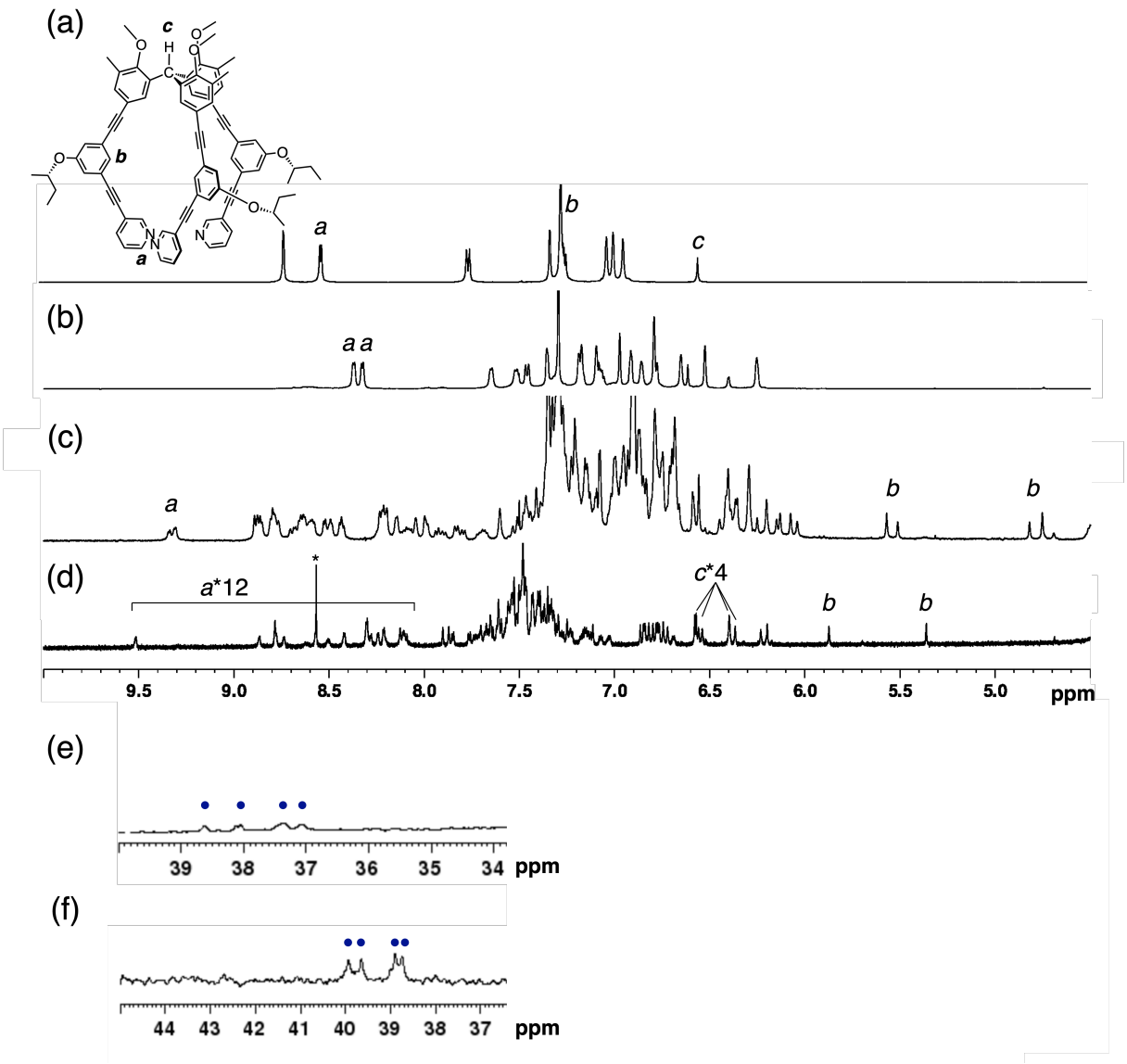


Figure S12. ^{1}H NMR (500 MHz, 300 K) spectra of (a) ligand **1b** (solvent: $CDCl_3$), (b) **2b** ($CDCl_3$/MeOD (97/3)), and (c) after the addition of $TBANO_3$ (1.5 equiv). (d) ^{1}H NMR (800 MHz, 283 K, CD_3NO_2) spectrum of cube **4a** (ligand: **1a**) for comparison.[S3] (e) ^{13}C NMR (201 MHz, 283 K) spectrum of (c) showing the signals for the central Ar_3C-H carbons. (f) ^{13}C NMR (201 MHz, 283 K) spectrum of (d) for comparison.[S3]

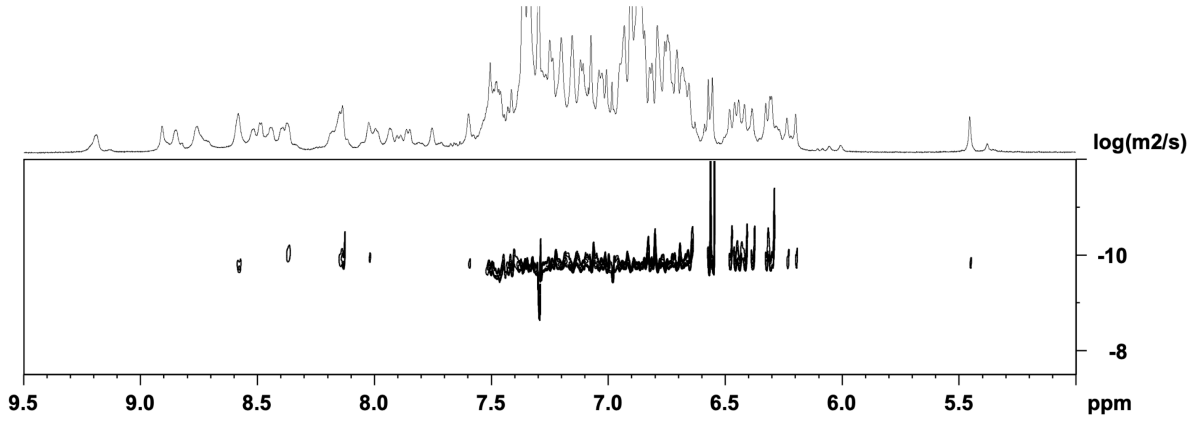


Figure S13. Representative ^{1}H DOSY NMR (500 MHz, $CDCl_3$/MeOD (97/3), 287 K) spectrum of cubic assembly **4c** (ligand: **1c**, 10 mM). Due to relatively low signal intensity, some of the peaks could not be detected despite the efforts to increase the concentration (**1c**: 2.5-20 mM).

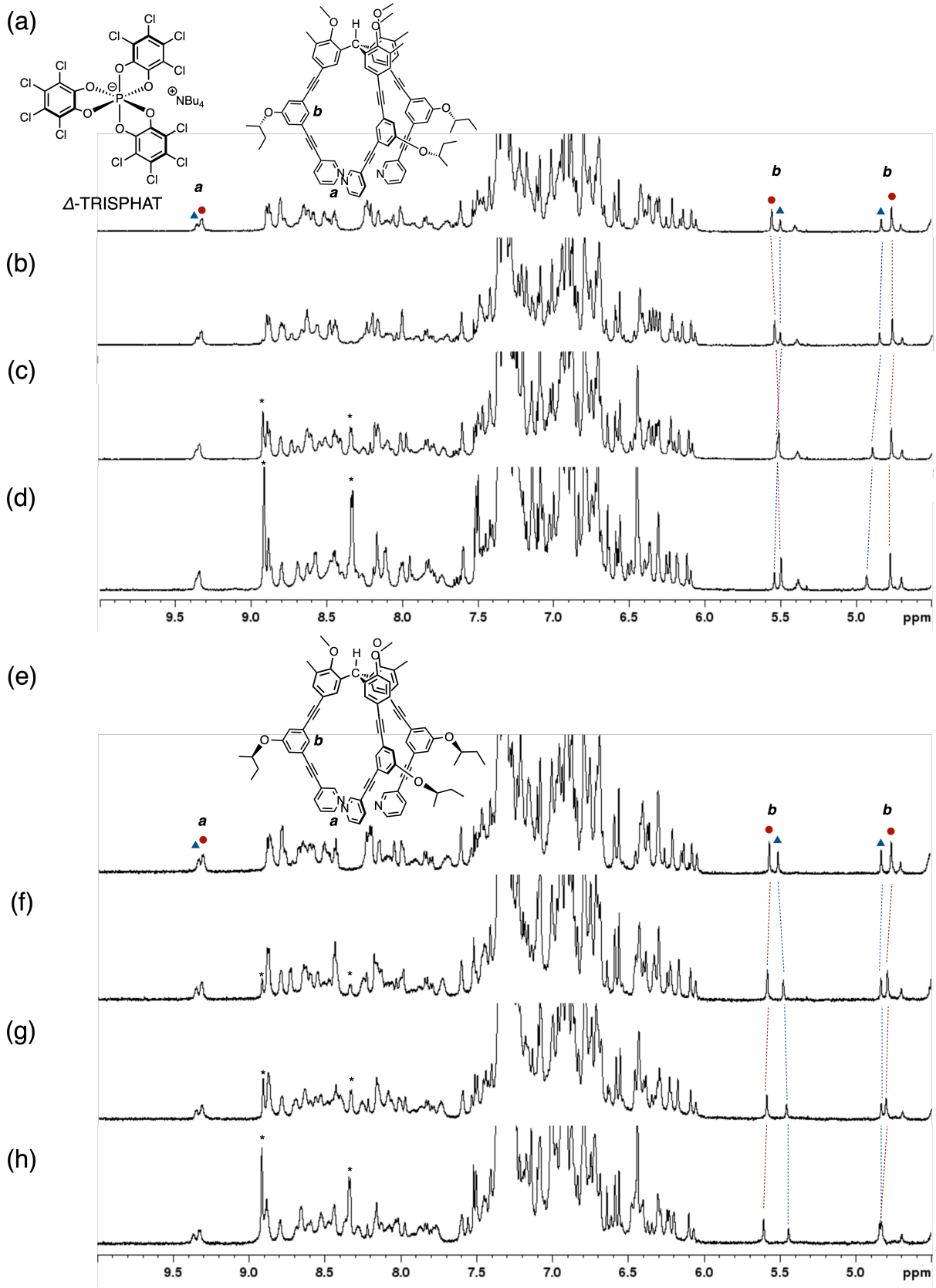


Figure S14. ^{1}H NMR (500 MHz, 287 K, $CDCl_3$/MeOD (97/3)) spectra of cube **4** upon addition of *Δ*-TRISPHAT. (a)-(d): Spectral changes of **4b** (ligand: (*S*)-**1b**, 2.5 mM) upon addition of 0 (a), 0.10 eq. (b), 0.20 eq. (c), 0.30 eq. (d). (e)-(h): Spectral changes of **4b** (ligand: (*R*)-**1b**, 2.5 mM) upon addition of 0 (e), 0.12 eq. (f), 0.24 eq. (g), 0.35 eq (h). Signals with asterisk are derived from partial dissociation due to the addition of anionic species.

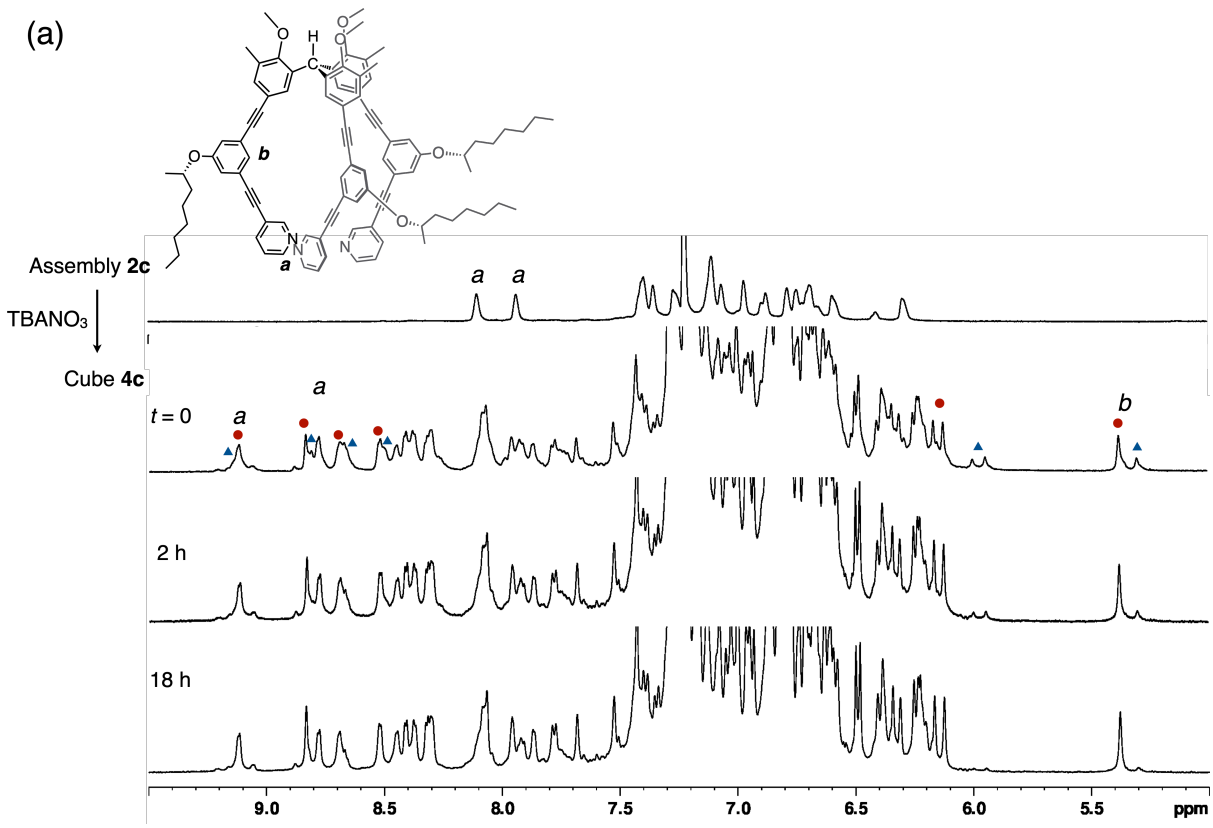


Figure S15. ^{1}H NMR (500 MHz, 287 K, $CDCl_3$/MeOD (97/3)) spectral changes upon interconversion of dimeric assembly **2c** (ligand: **1c**) to cube **4c**.

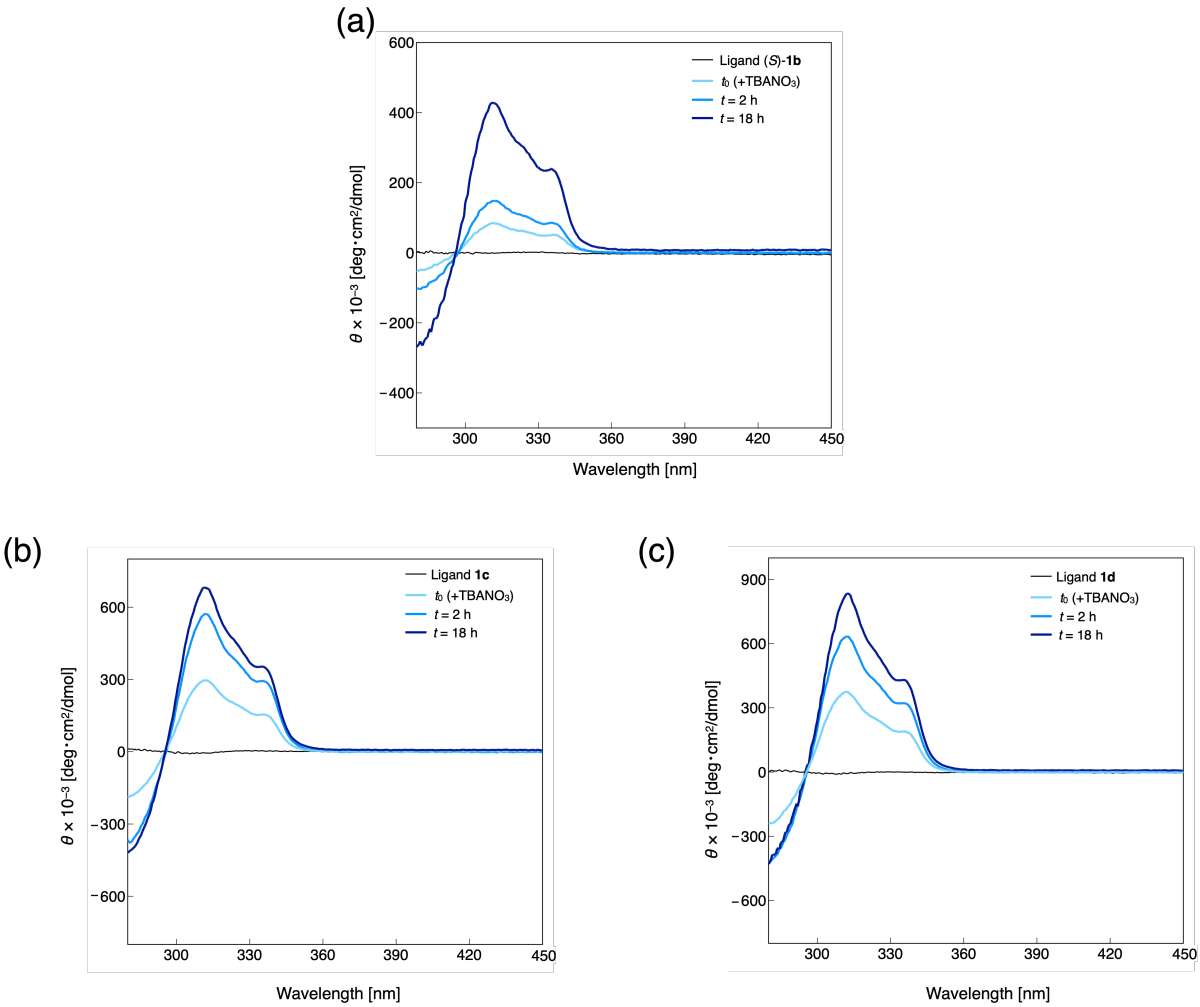


Figure S16. CD (293 K, $CHCl_3$/MeOD (97/3), ligand: 0.125 mM) spectral changes upon (a) interconversion of assembly **2b** (ligand: **1b**) to cube **4b**, (b) interconversion of assembly **2c** (ligand: **1c**) to cube **4c**, and (c) interconversion of assembly **2d** (ligand: **1d**) to cube **4d**.

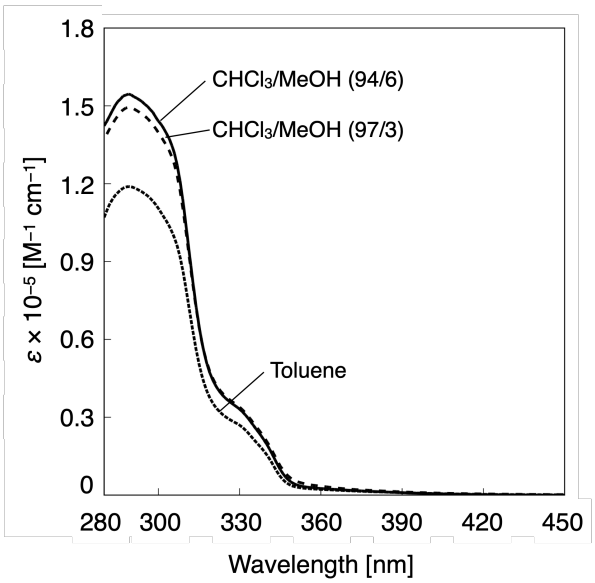


Figure S17. UV-vis absorption spectra (293 K) of ligand **1b** in different solvents.

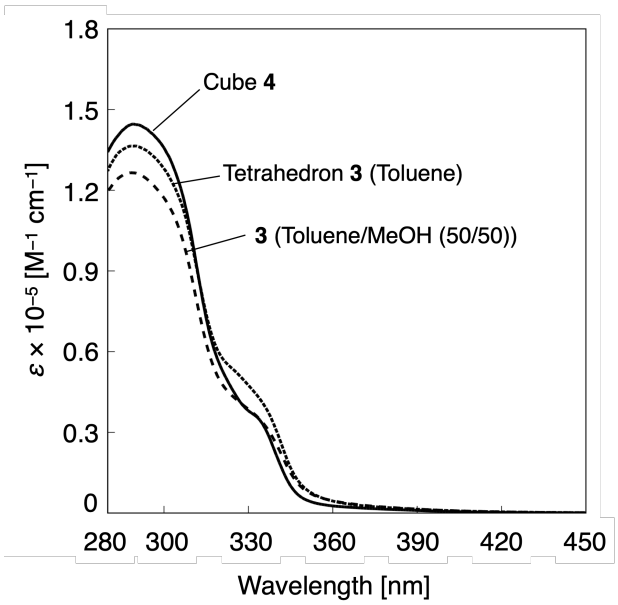


Figure S18. UV-vis absorption spectra (293 K) of cube **4b** (ligand: **1b**, silver salt: $AgPF_6$ (then treated with $TMANO_3$ and stored for 18 h at rt)) in $CHCl_3$/MeOH (94/6) and tetrahedron **3b** (ligand: **1b**) in varied solvents.

3. Supplementary crystallographic analysis

Single crystals of $(M_3L_2)_2$ cage **2b** (L: (*S*)-**1b**) were prepared by vapor diffusion of diethyl ether into a CD_3NO_2 solution of the complex (with BF_4^- as the counter anion) at 283 K over a week (Figure S19). The diffraction data were collected at the BL26B1 beamline (EIGER 4M (DECTRIS) detector) at Spring-8. The crystals were removed from the microtubes and introduced into a glass capillary (borosilicate, Hampton Research), and mounted on a goniometer. Data collection was performed at 100 K. XDS[S6] was used for the processing and data reduction. The structures were solved and refined by SHELXT[S7] and SHELXL.[S8] Disorders of counter ions and solvent molecules were severe thus treated with PLATON/SQUEEZE protocol.[S9] Detailed crystallographic data are summarized in Table S1. PyMOL 2.0 (Schrödinger, LLC) was used for the production of graphics.

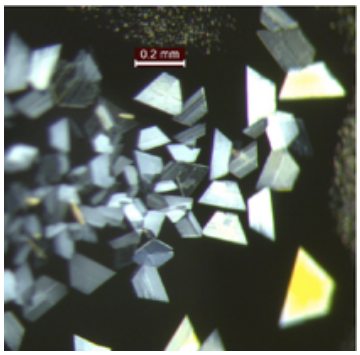


Figure S19. Crystal photograph of cage **2b**.

Table S1. Crystal data and structure refinement for cage **2b**.

	2b
Identification code	sh517-5-crystal02_a_sqd
CCDC number	2108704
Empirical formula	$C_{1220}H_{968}N_{52}O_{104}B_{11.95}F_{47.82}Cu_{24}$
Formula weight	20583.18
Temperature	100(2) K
Wavelength	1.000 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimension	a = 18.838(4) Å, b = 32.458(6) Å, c = 64.439(13) Å $\alpha = \gamma = 90°$, β = 94.55(3)°
Volume	39277(14) Å^3
Z	1
Density (calculated)	0.870 g/cm^3
Absorption coefficient	0.920 mm^{-1}
F(000)	10670
θ range for data collection	1.784 to 47.56°
Index ranges	$-14 \leqq h \leqq 14$ $-26 \leqq k \leqq 26$ $-51 \leqq l \leqq 51$
Reflection collected	69369
Independent reflections	20892 [R_{int} = 0.1010]
Data / restrains / parameters	20892 / 5744 / 3100
Goodness-of-fit on F^2	1.290
Final R indices [$I>2\sigma(I)$]	R_1 = 0.1440 wR_2 = 0.3746
R indices (all data)	R_1 = 0.1935 wR_2 = 0.4105
Largest diff. peak and hole	0.39 and −0.61 e Å^{-3}

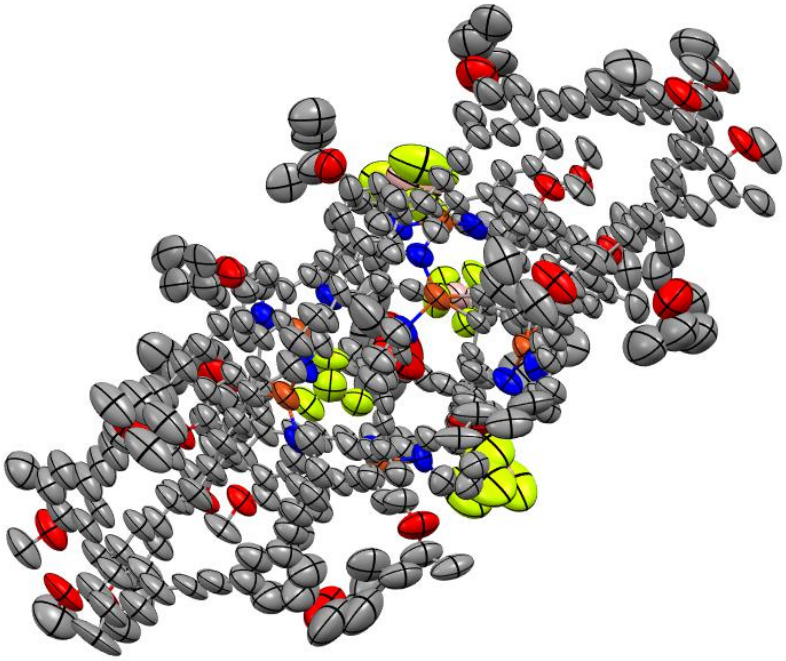


Figure S20. ORTEP drawing (50% probability ellipsoids) of assembly **2b**. Hydrogen atoms are omitted for clarity.

4. References

[S1] Y. Domoto, M. Abe, T. Kikuchi, M. Fujita, *Angew. Chem. Int. Ed.* **2020**, *59*, 3450-3454.

[S2] J. Kobayashi, Y. Domoto, T. Kawashima, *Chem. Commun.* **2009**, 6186-6188.

[S3] Y. Domoto, M. Abe, M. Fujita, *J. Am. Chem. Soc.* **2021**, *143*, 8578-8582.

[S4] F. J. V. Santos, C. A. N. de Castro, J. H. Dymond, N. K. Dalaouti, M. J. Assael, A. Nagashima, *J. Phys. Cgem. Ref. Data* **2006**, *35*, 1-8.

[S5] (a) T. Yamada, Y. Nagata, M. Suginome, *Chem. Commun.* **2010**, *46*, 4914-4916; (b) Y. Nagata, T. Yamada, T. Adachi, Y. Akai, T. Yamamoto, M. Suginome, *J. Am. Chem. Soc.* **2013**, *135*, 10104-10113.

[S6] W. Kabsch, *Acta Crystallogr. D* **2010**, *66*, 125-132.

[S7] G. M. Sheldrick, *Acta Crystallogr. A* **2015**, *71*, 3-8.

[S8] G. M. Sheldrick, *Acta Crystallogr. C* **2015**, *71*, 3-8.

[S9] A. L. Spek, *J. Appl. Cryst.* **2003**, *36*, 7-13.

5. Representative NMR spectra of the $(M_3L_2)_n$ polyhedra

5.1 NMR spectra of the $(Cu_3((S)\text{-}1b)_2)_2$ complex (2b, BF_4^- salt)

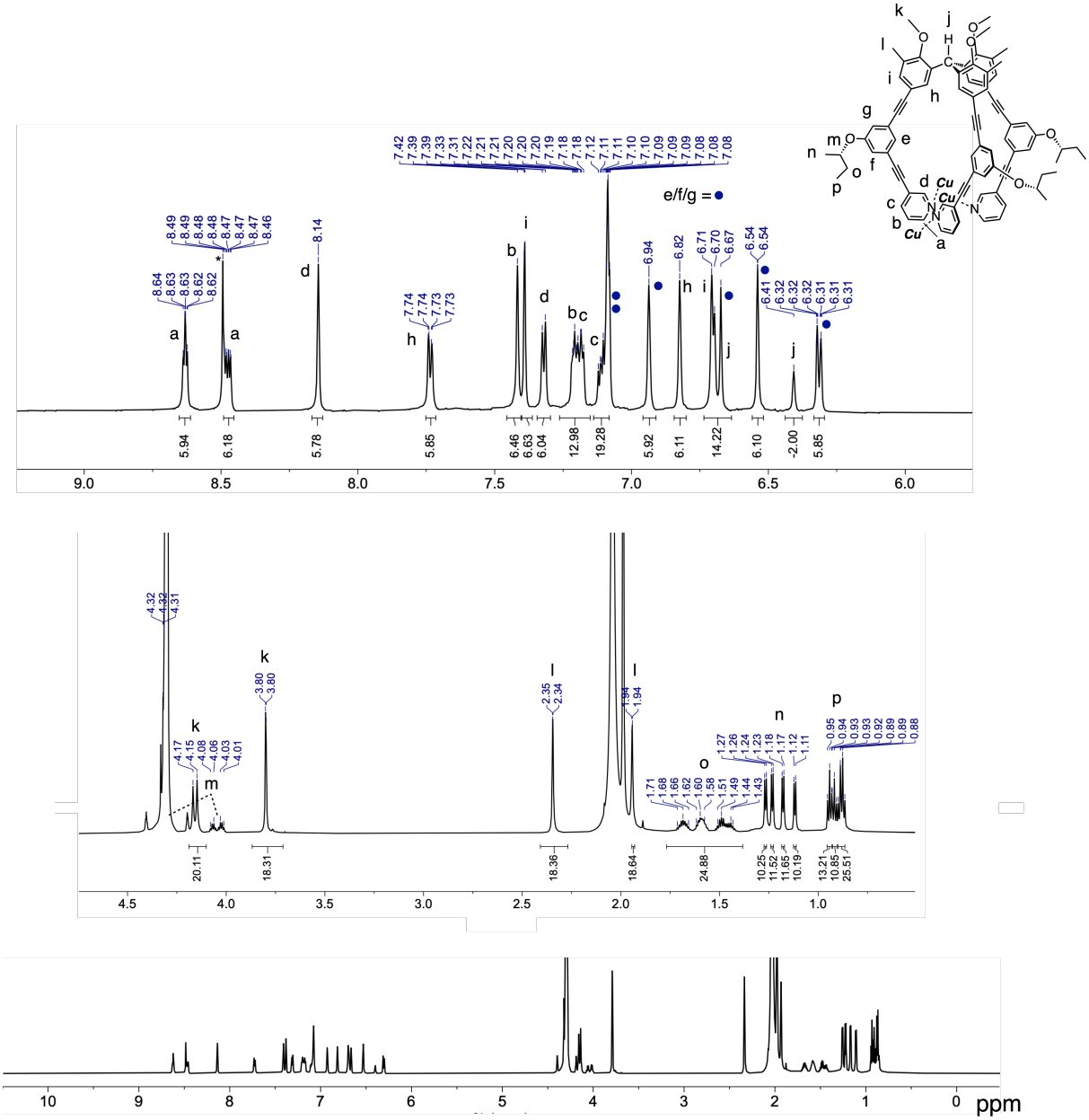


Figure S21. ^{1}H NMR (700 MHz, CD_3NO_2, 300 K) spectrum of $[(Cu_3((S)\text{-}\mathbf{1b})_2)_2](BF_4)_6$.

Firstly, two sets of the signals are observed derived from the *outer* and *inner* ligands in the $Cu_3(\mathbf{1b})_2$ subunit constituting the framework of **2b**. Existence of two diastereomers (~50:50) resulted in the furthermore splitting, while integral values were shown in combined total for clarity.

* H_e, H_f and H_g could not be distinguished.

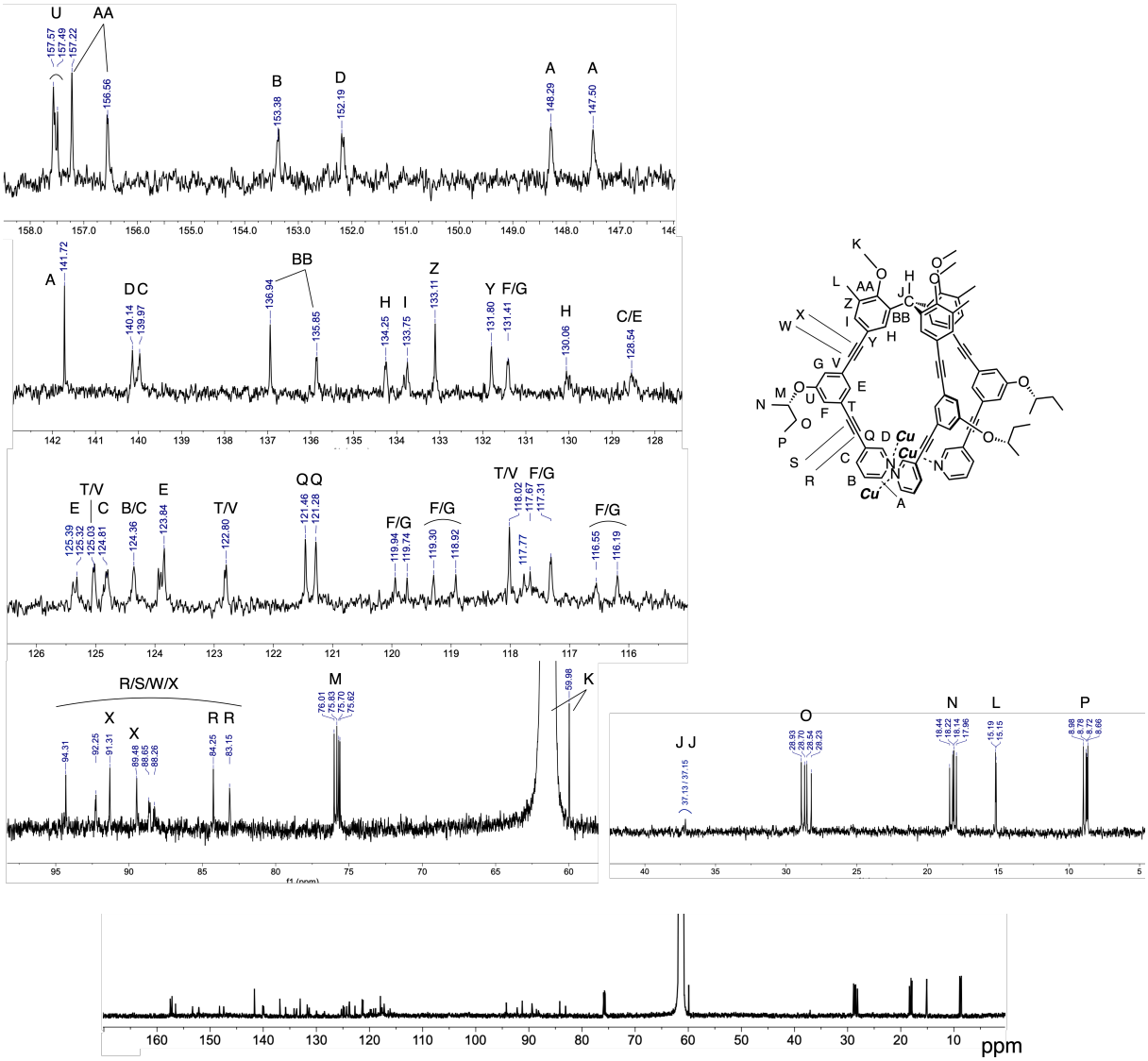


Figure S22. ^{13}C NMR (176 MHz, CD_3NO_2, 300 K) spectrum of **2b**.

Assignment could be partly done because of severe overlap between different carbon signals and the existence of diastereomers of **2b** with ~50:50 ratio.

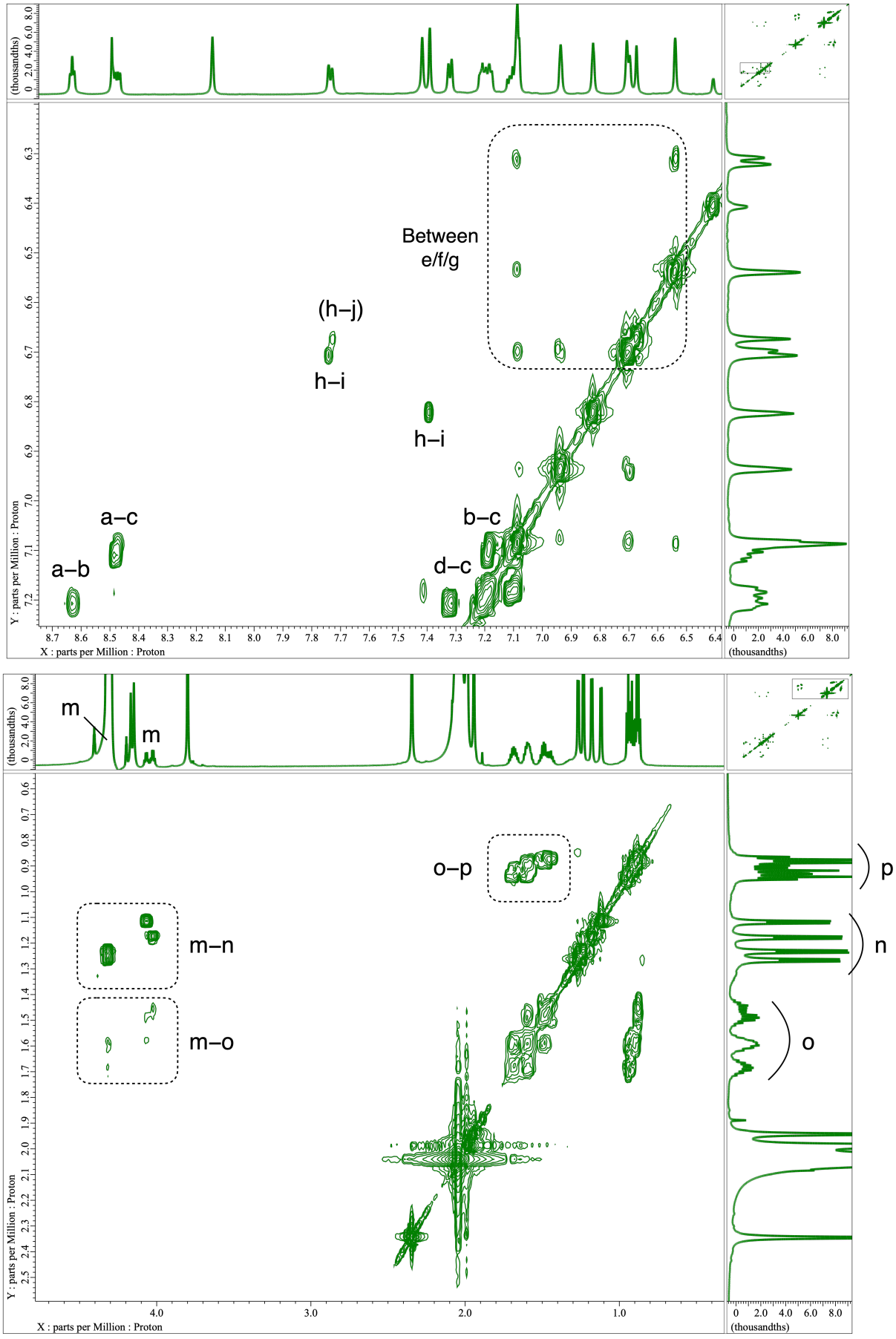


Figure S23. $^{1}H–^{1}H$ COSY (700 MHz, CD_3NO_2, 300 K) spectrum of **2b**.

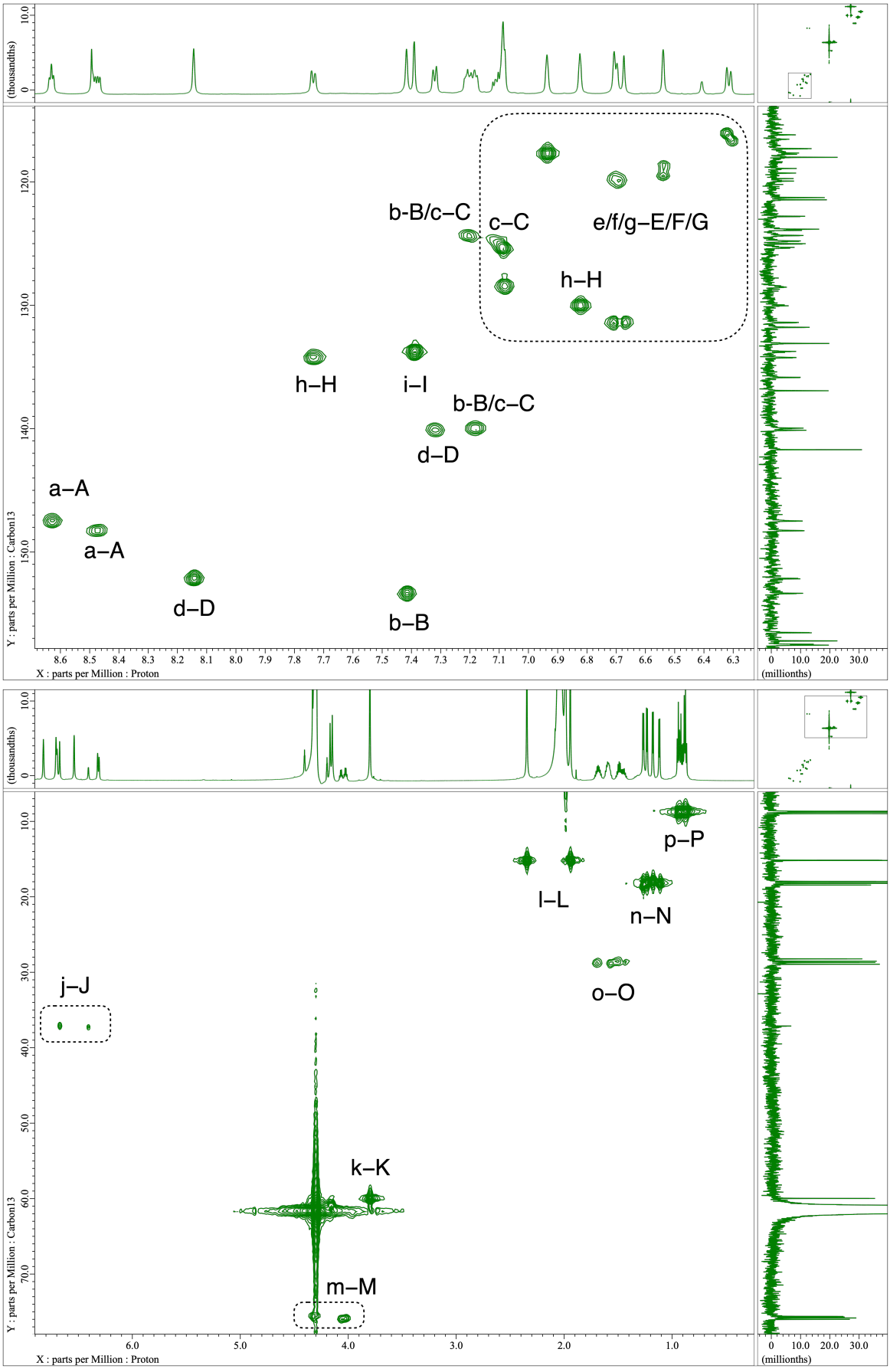


Figure S24. $^{1}H–^{13}C$ HMQC (CD_3NO_2, 300 K) spectrum of **2b**.

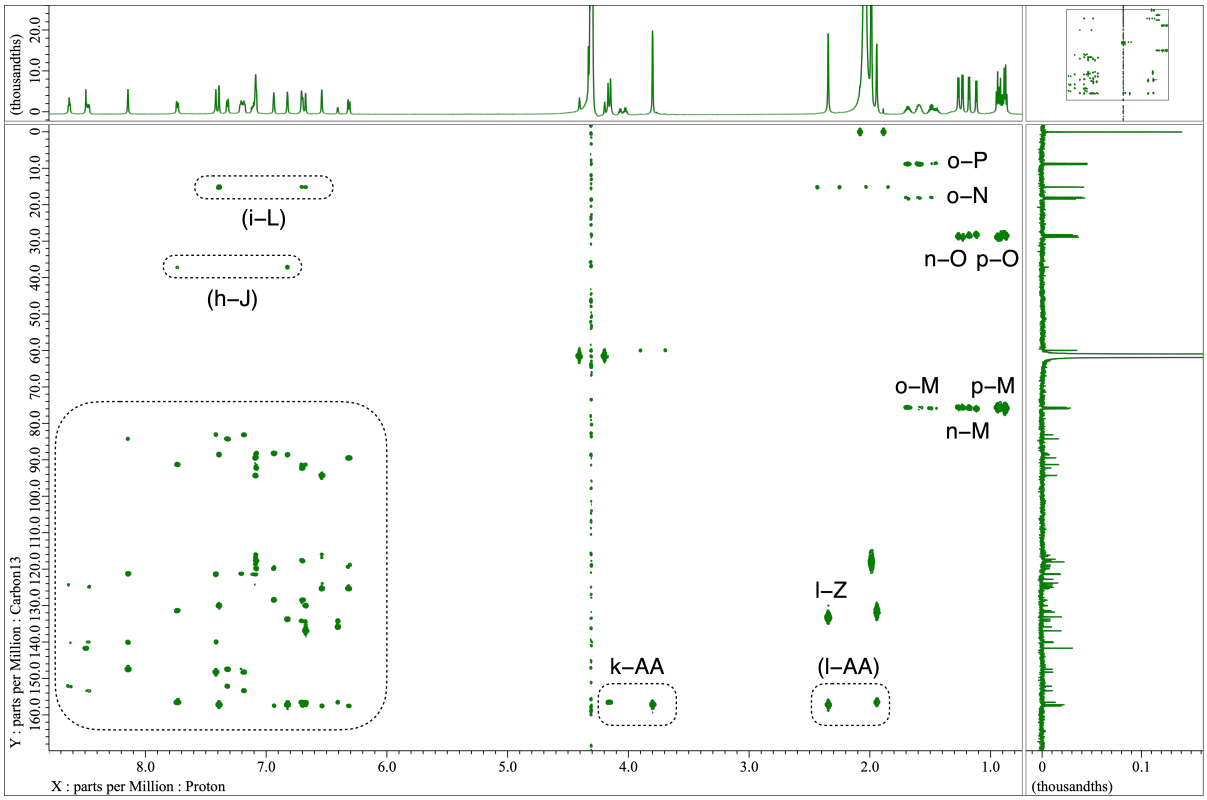


Figure S25. ^{1}H–^{13}C HMBC (CD_3NO_2, 300 K) spectrum of **2b**.

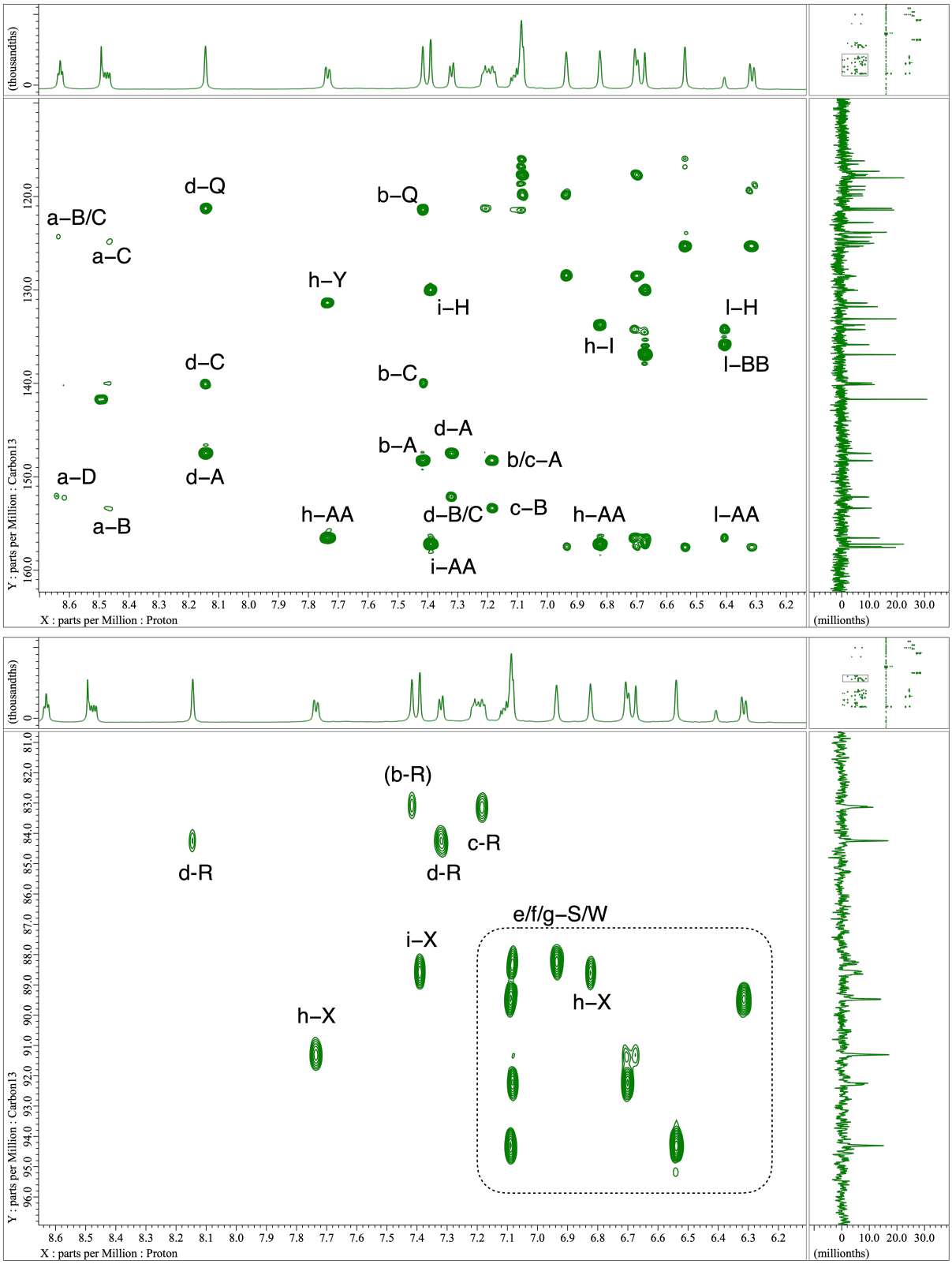
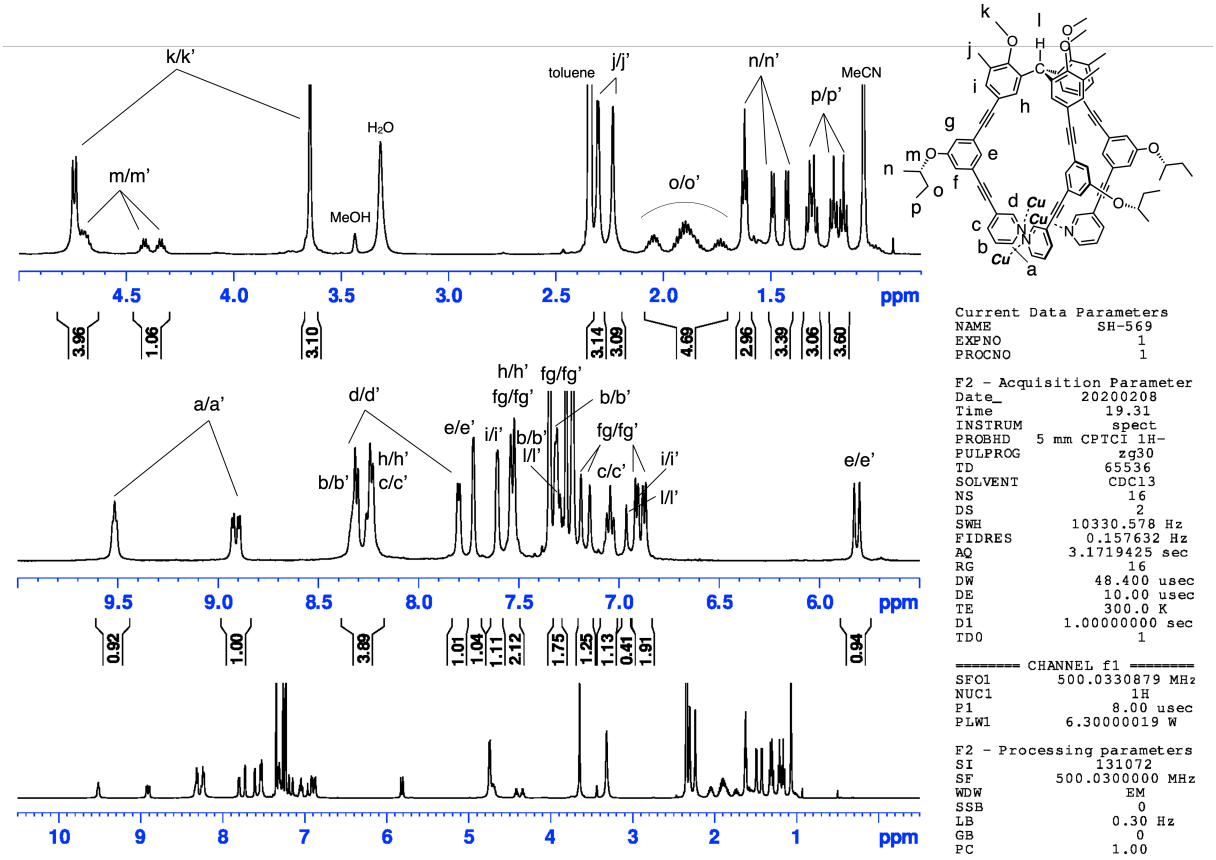


Figure S26. Partly magnified $^{1}H–^{13}C$ HMBC (CD_3NO_2, 300 K) spectrum of **2b**.

5.2 NMR spectra of the $(Cu_3((S)\text{-}1b)_2)_4$ tetrahedron (3b, BF_4^- salt)

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EXPNO                      1
PROCNO                     1

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Time                 19.31
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PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             10330.578 Hz
FIDRES           0.157632 Hz
AQ               3.1719425 sec
RG                     16
DW                  48.400 usec
DE                  10.00 usec
TE                  300.0 K
D1               1.00000000 sec
TD0                    1

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NUC1                  1H
P1                 8.00 usec
PLW1          6.30000019 W

F2 - Processing parameters
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SF            500.0300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
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Figure S27. ^{1}H NMR (500 MHz, toluene-d_8/MeOD (94/6), 300 K) spectrum of **3b**.

Firstly, two sets of the signals are observed derived from the *outer* and *inner* ligands in the Cu_3L_2 subunit constituting the tetrahedral framework of **3**. Existence of two diastereomers (47:53 under this condition shown as *x/x'* for each signal) resulted in the furthermore peak splitting, while integral values were shown in combined total for clarity. *H_f and H_g could not be distinguished.

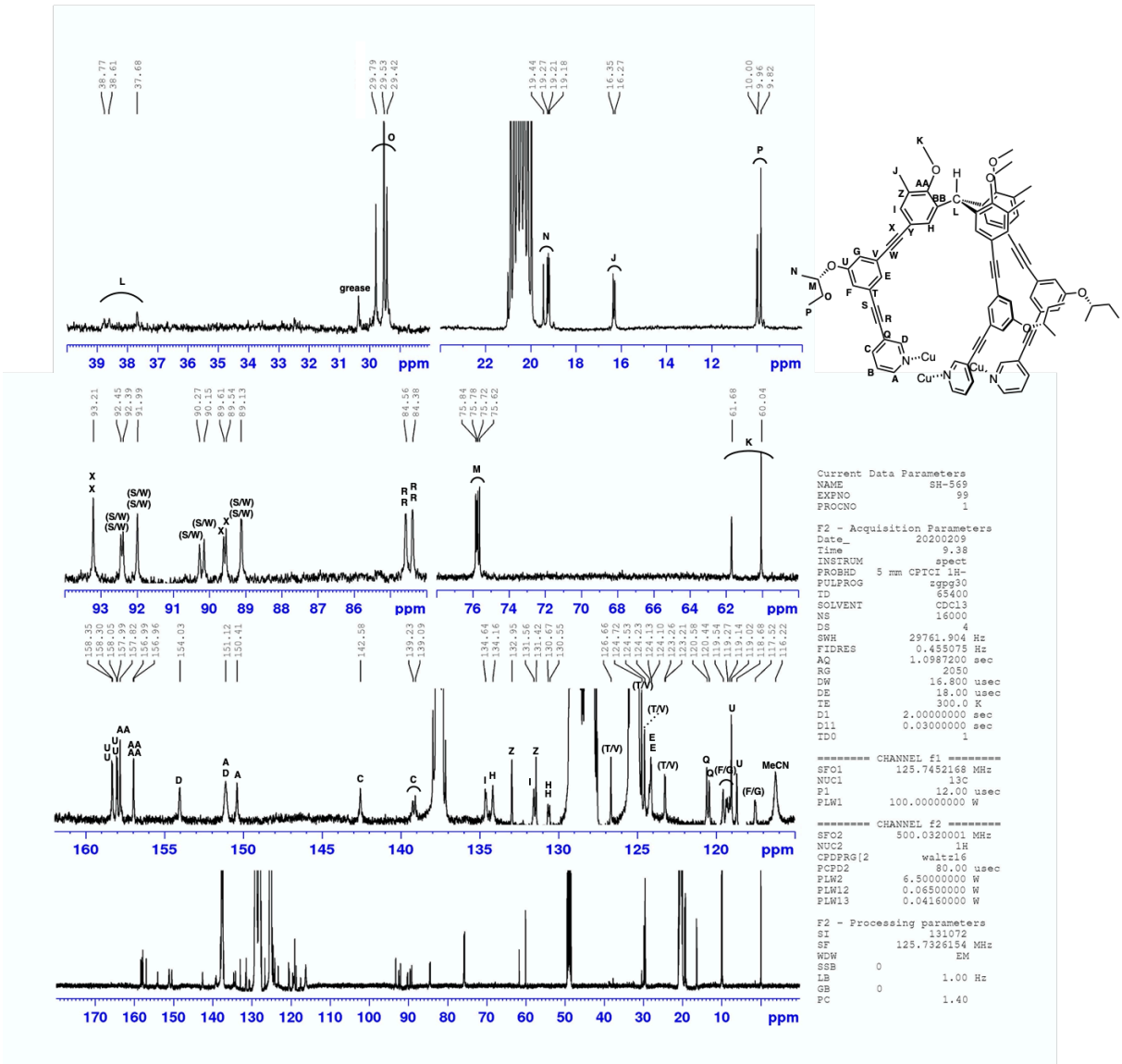

Figure S28. ^{13}C NMR (126 MHz, toluene-d_8/MeOD (94/6), 300 K) spectrum of **3b**.

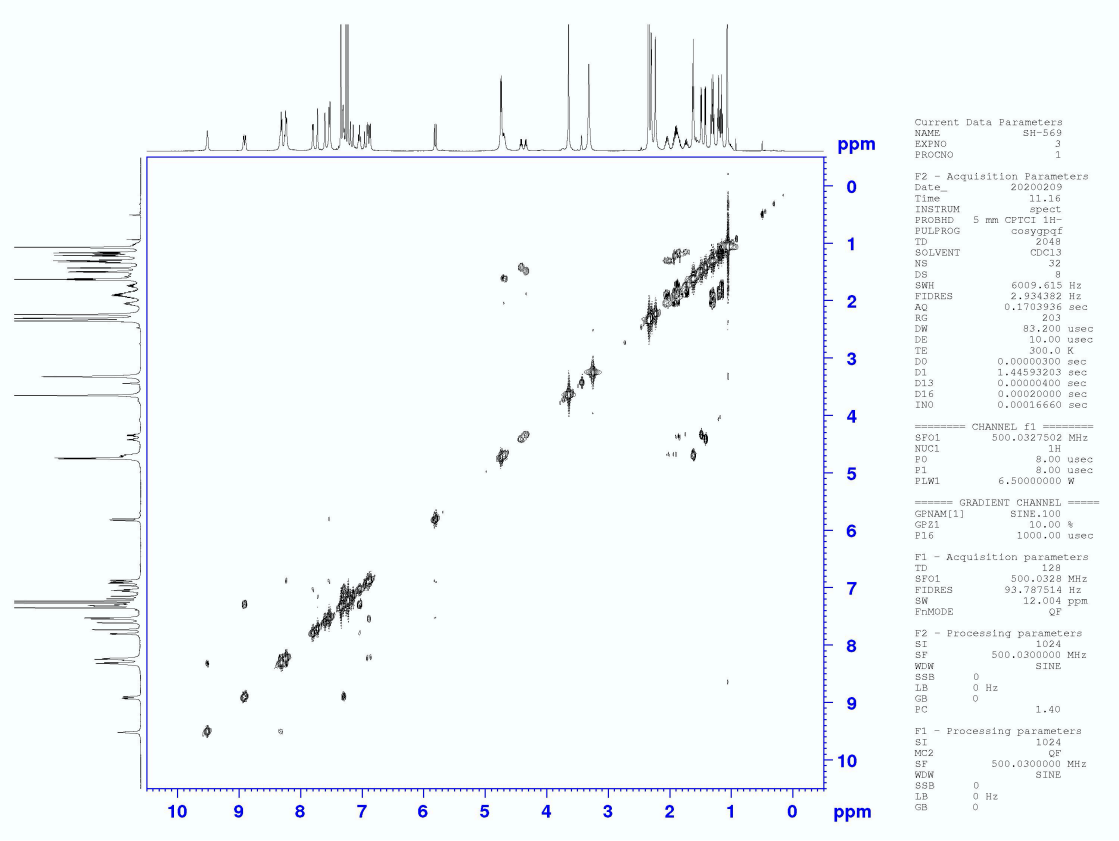

Figure S29. ^{1}H–^{1}H COSY NMR (500 MHz, toluene-d_8/MeOD (94/6), 300 K) spectrum of **3b**.

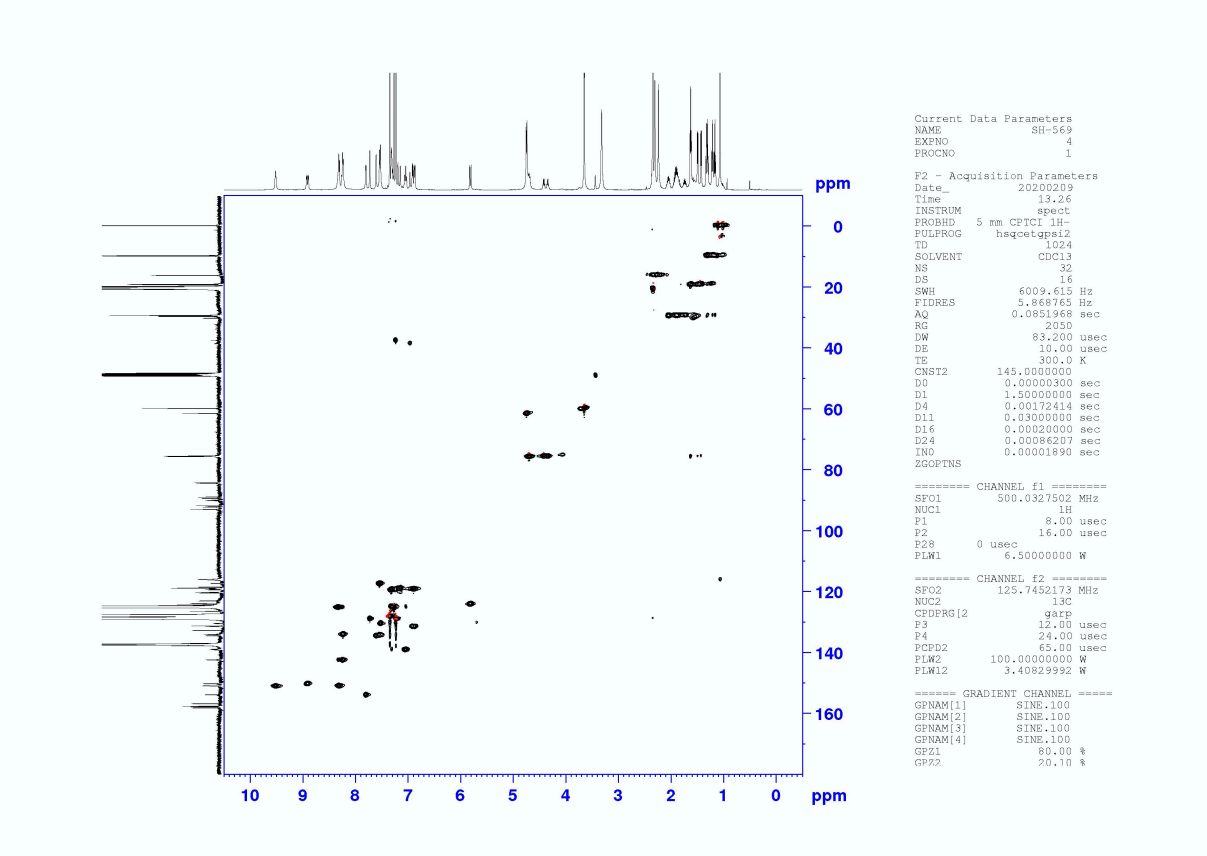

Figure S30. ^{1}H–^{13}C HSQC NMR (toluene-d_8/MeOD (94/6), 300 K) spectrum of **3b**.

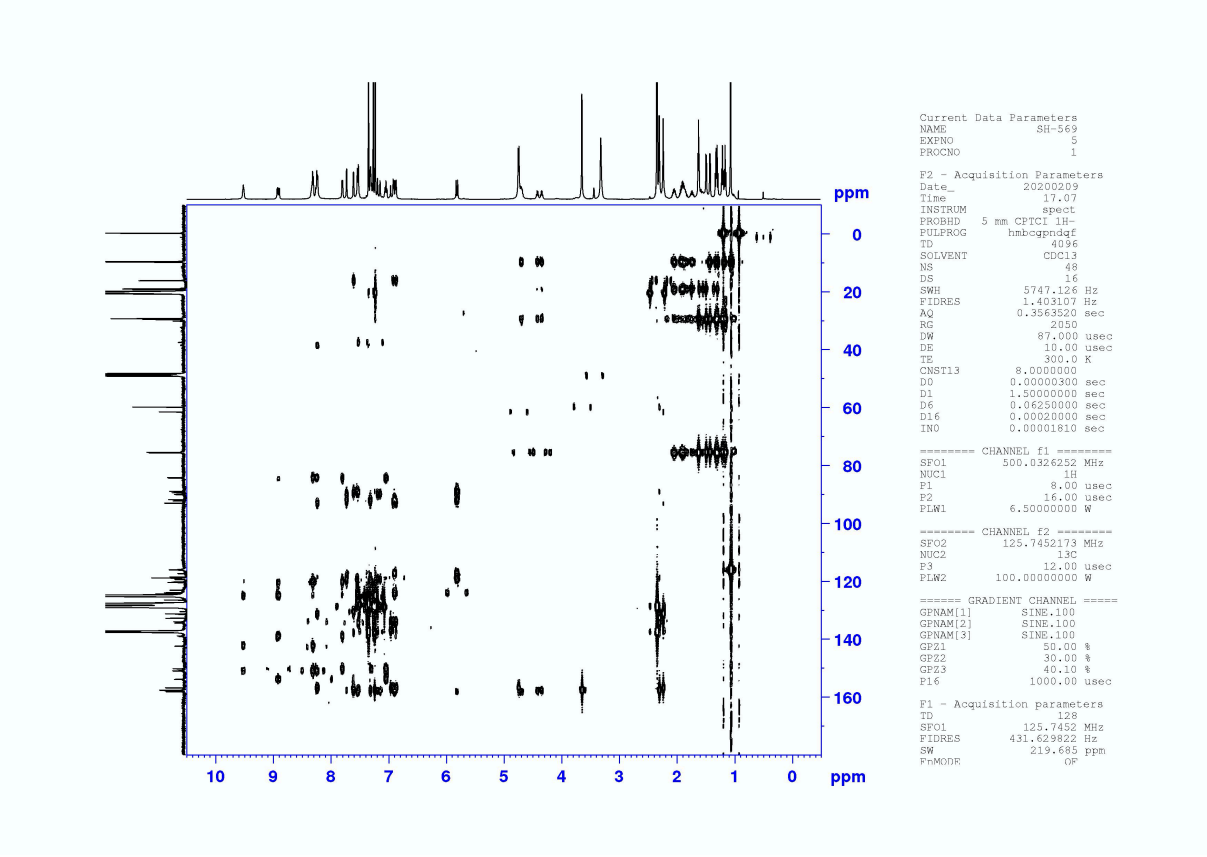

Figure S31. ^{1}H–^{13}C HMBC NMR (toluene-d_8/MeOD (94/6), 300 K) spectrum of **3b**.

5.3 NMR spectra of the $(Ag_3((S)\text{-}1b)_2)_8$ cube (4b)

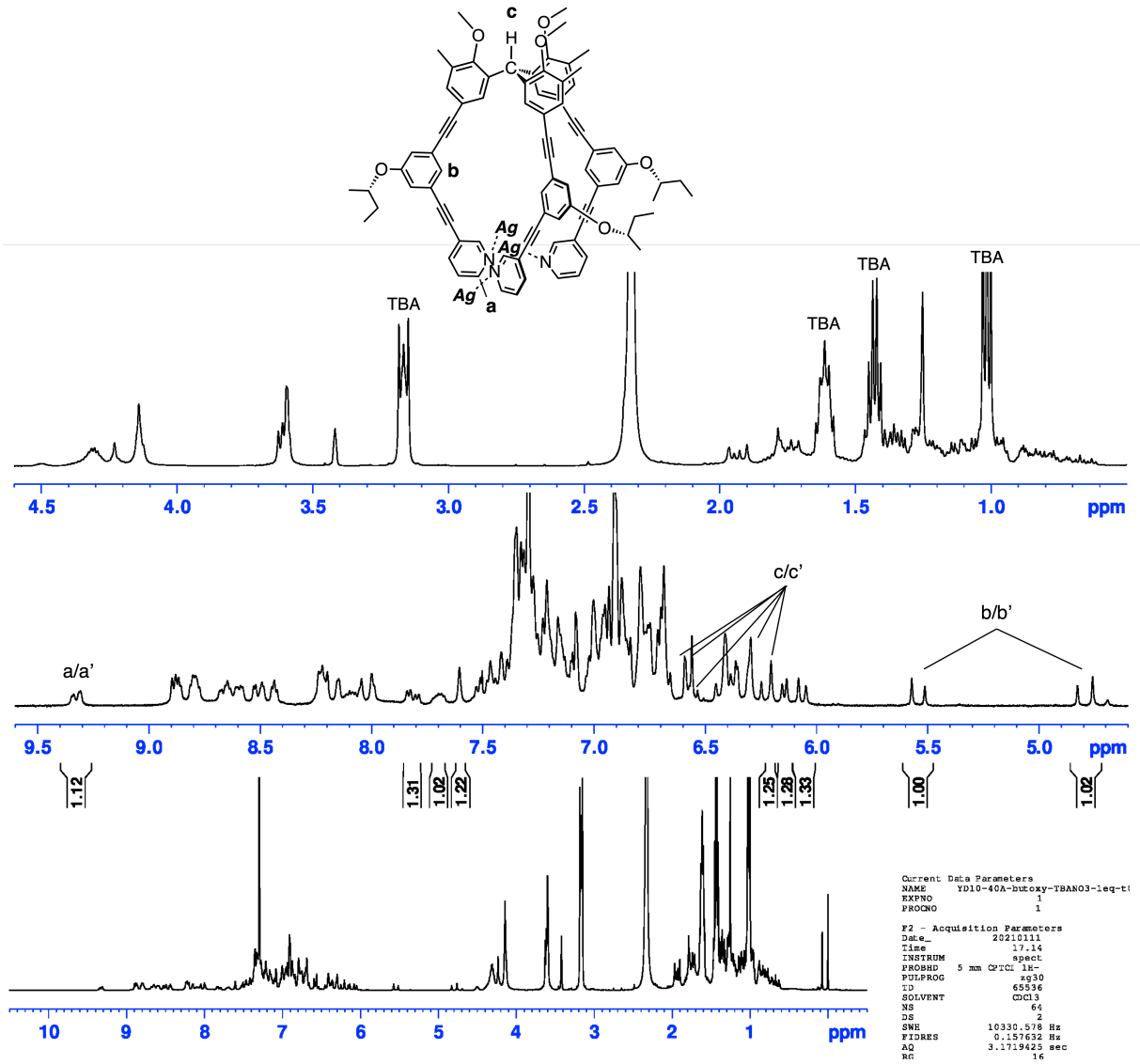

Figure S32. ^{1}H NMR (500 MHz, $CDCl_3$/MeOD (97/3), 287 K) spectrum of cubic assembly **4b**, containing $TBANO_3$ added for interconversion.

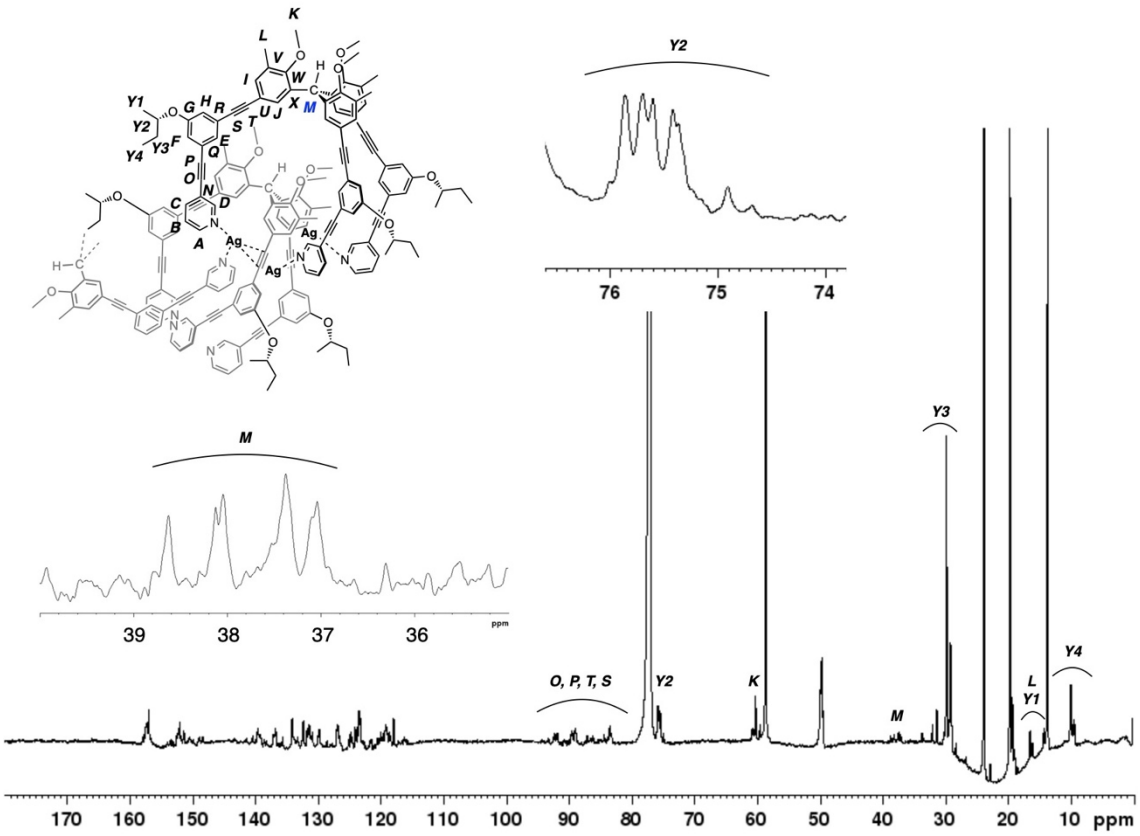

Figure S33. ^{13}C NMR (201 MHz, $CDCl_3$/MeOD (97/3), 283 K) spectrum of the octameric cube **4b**, containing $TBANO_3$ added for interconversion.

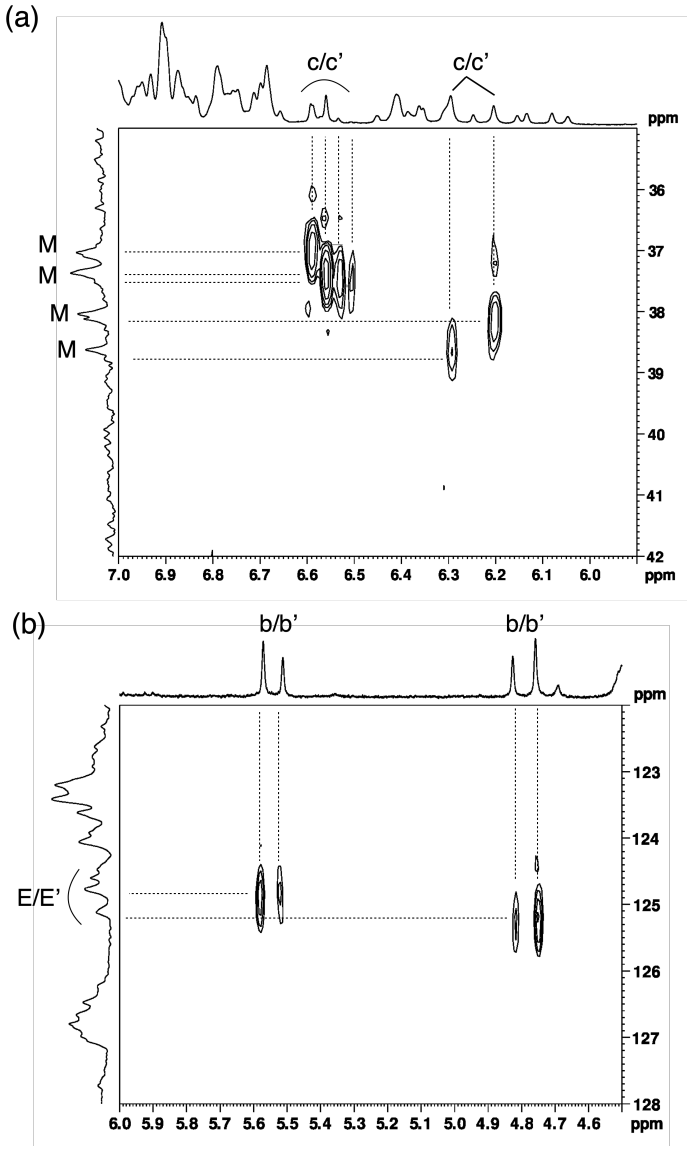

Figure S34. Partial $^{1}H–^{13}C$ HSQC ($CDCl_3/CD_3OD$ (97/3), 283 K) spectrum of **4b**. (a) the correlation between central Ar_3C-*H* protons and their counterpart methyn carbons. Some of H_m and C_M signals for minor isomer are overlapped and unidentified, (b) the correlation between two peaks of H_b at around 5 ppm and their counterpart carbons (C_E).

6. NMR data of synthesized materials

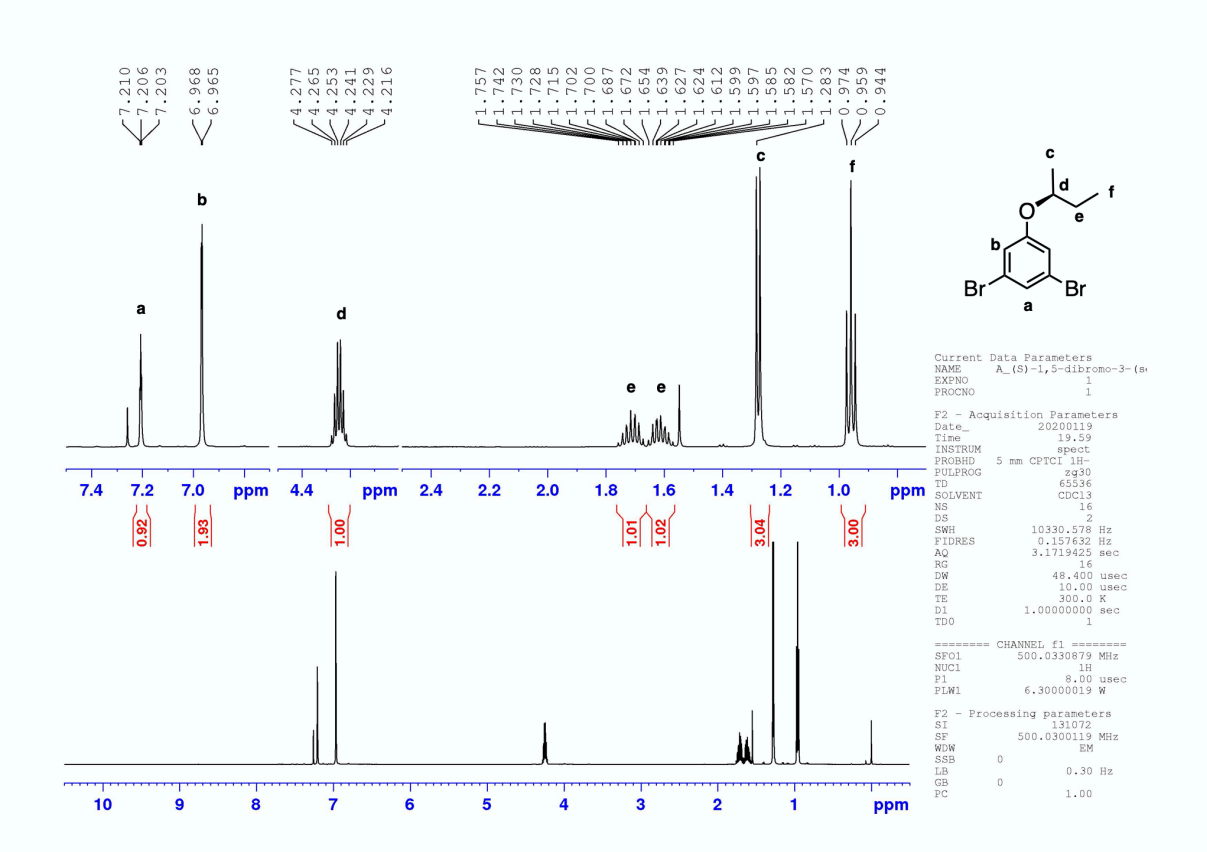

Figure S35. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **S1**.

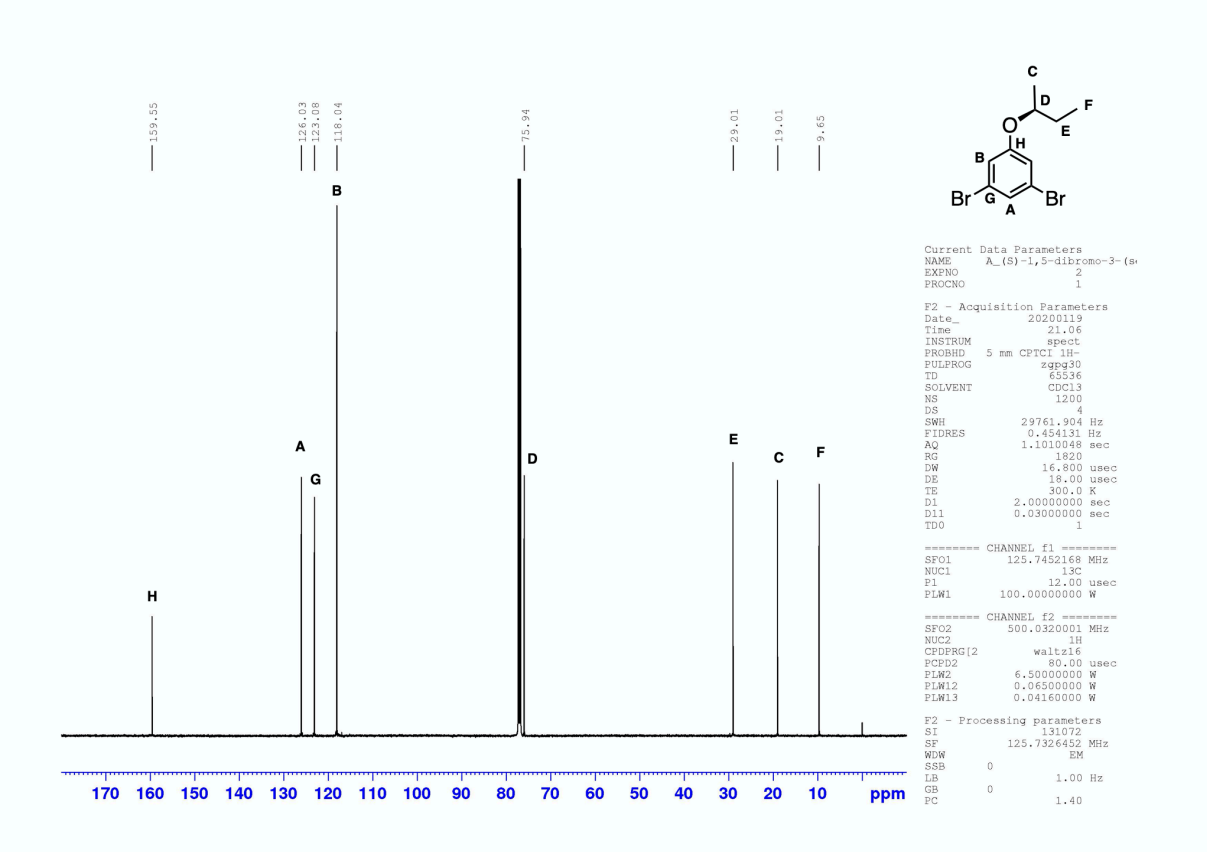

Figure S36. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **S1**.

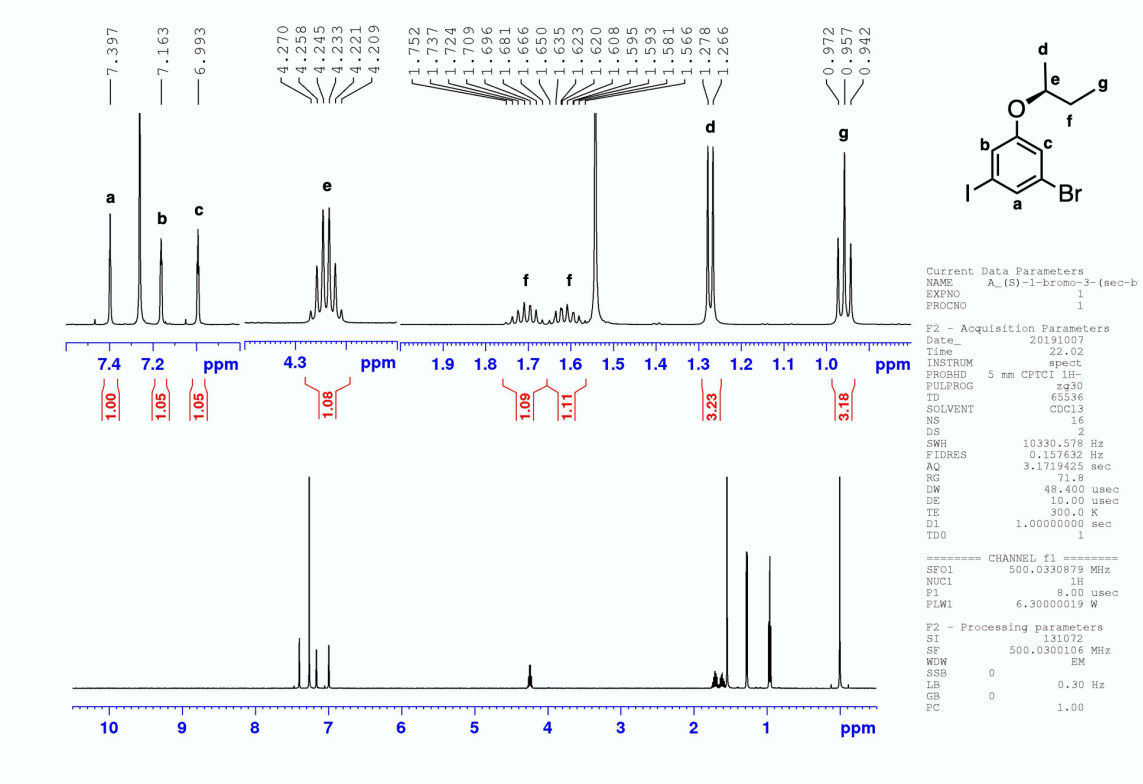

Figure S37. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **S2**.

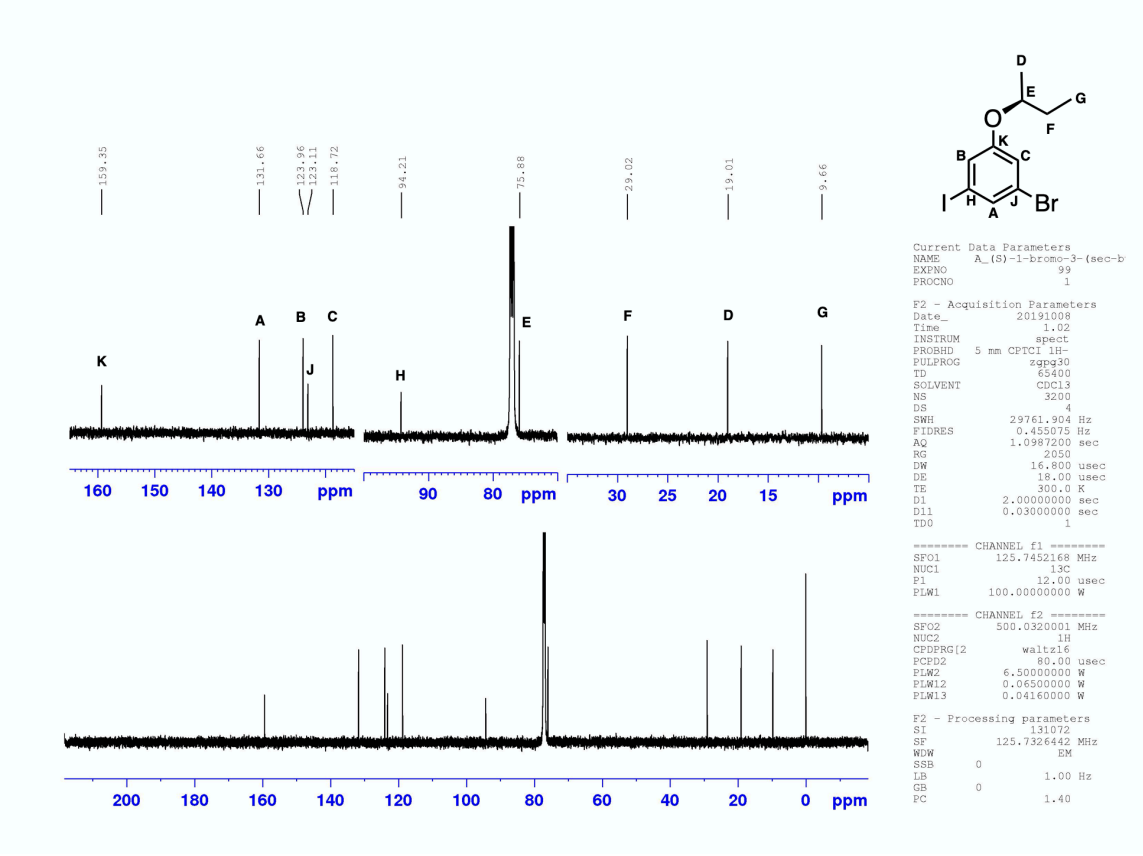

Figure S38. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **S2**.

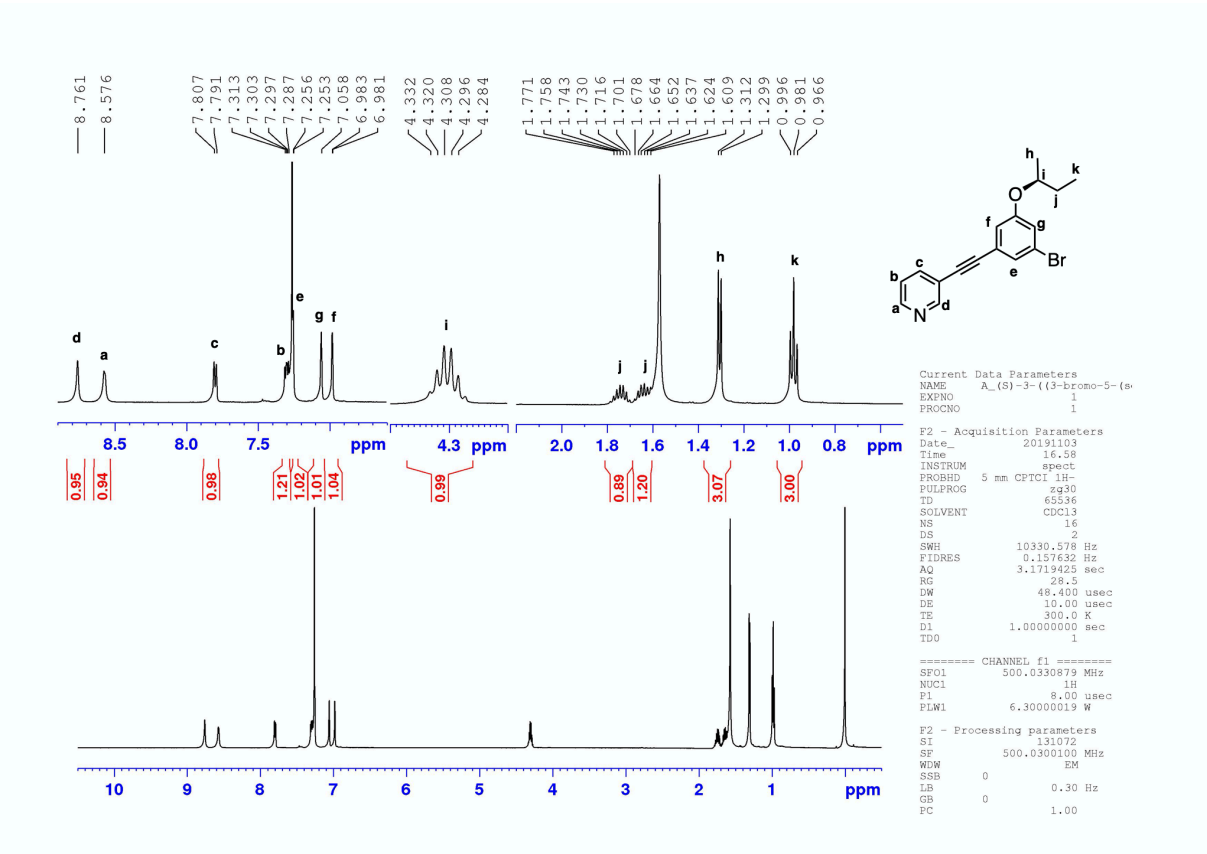

Figure S39. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **S3**.

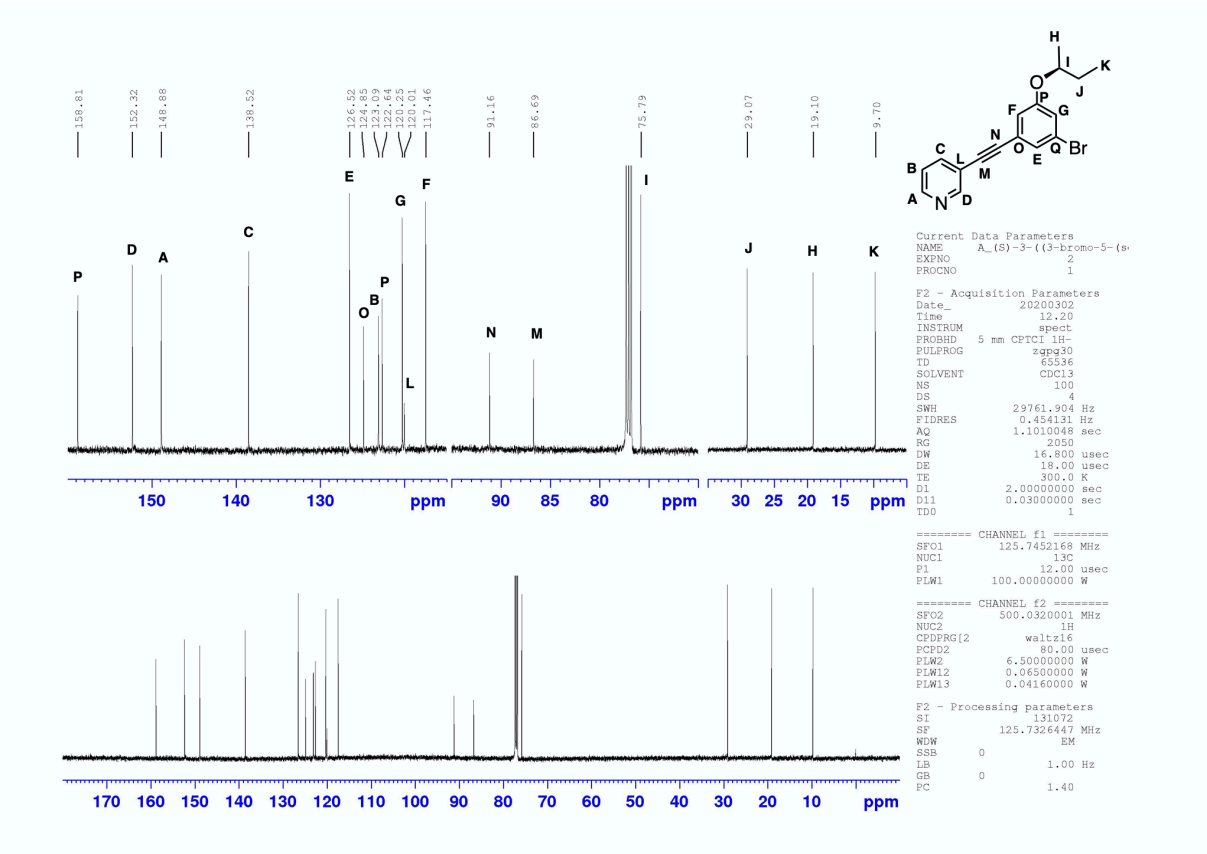

Figure S40. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **S3**.

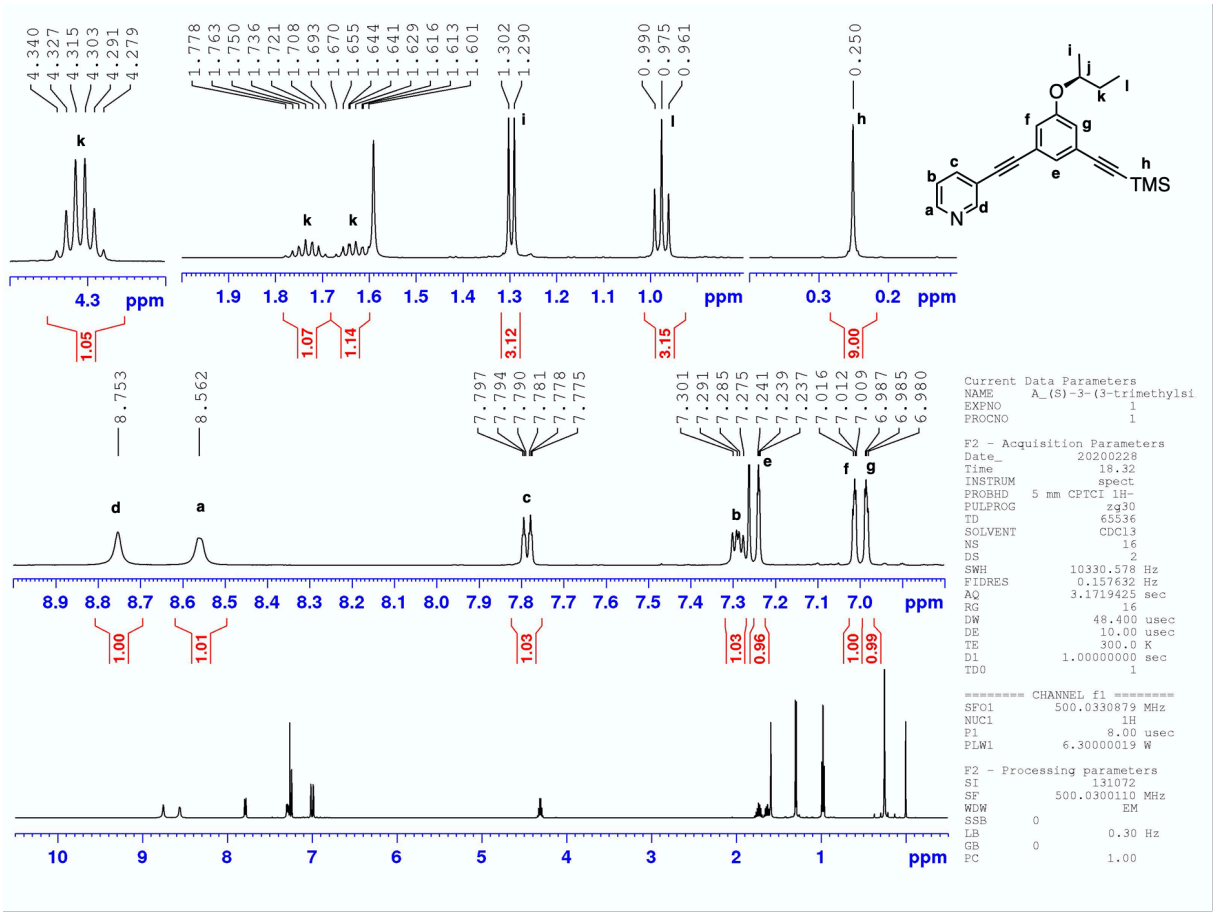

Figure S41. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **S4**.

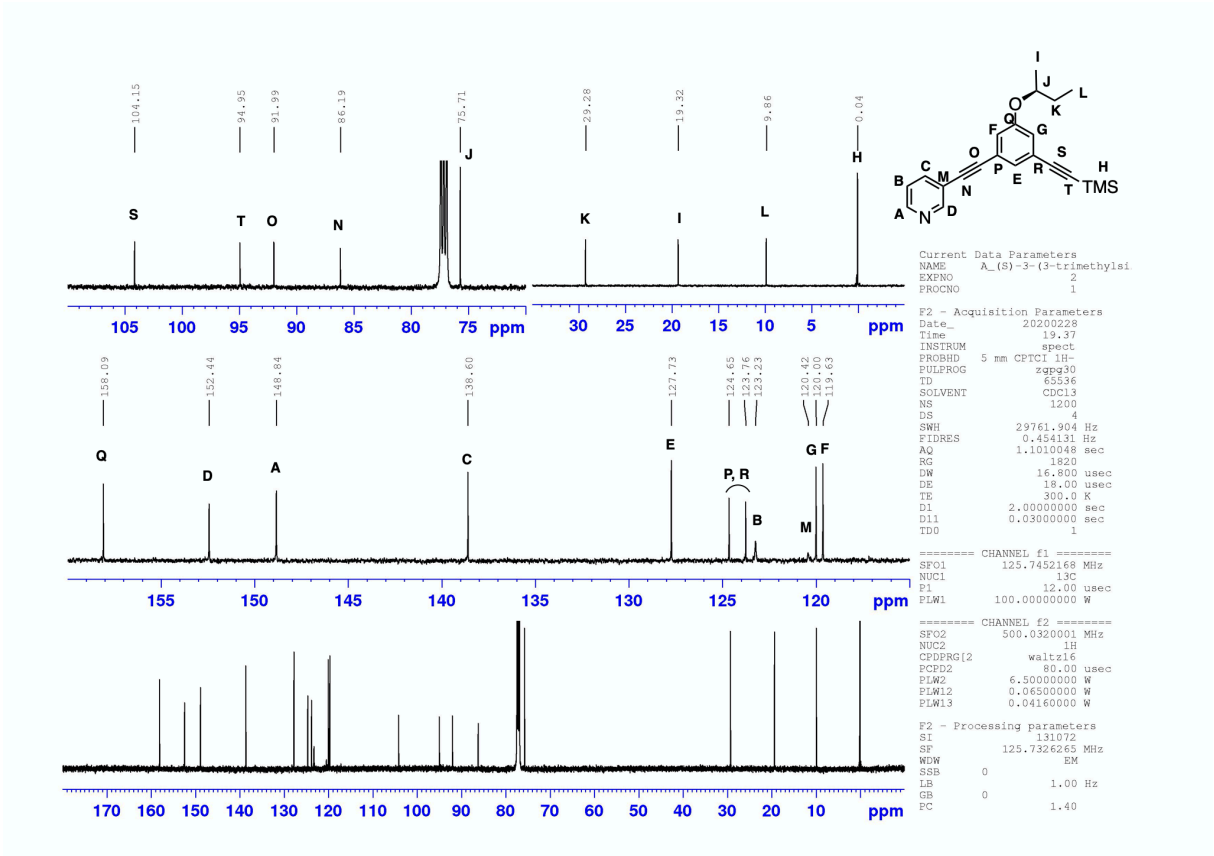

Figure S42. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **S4**.

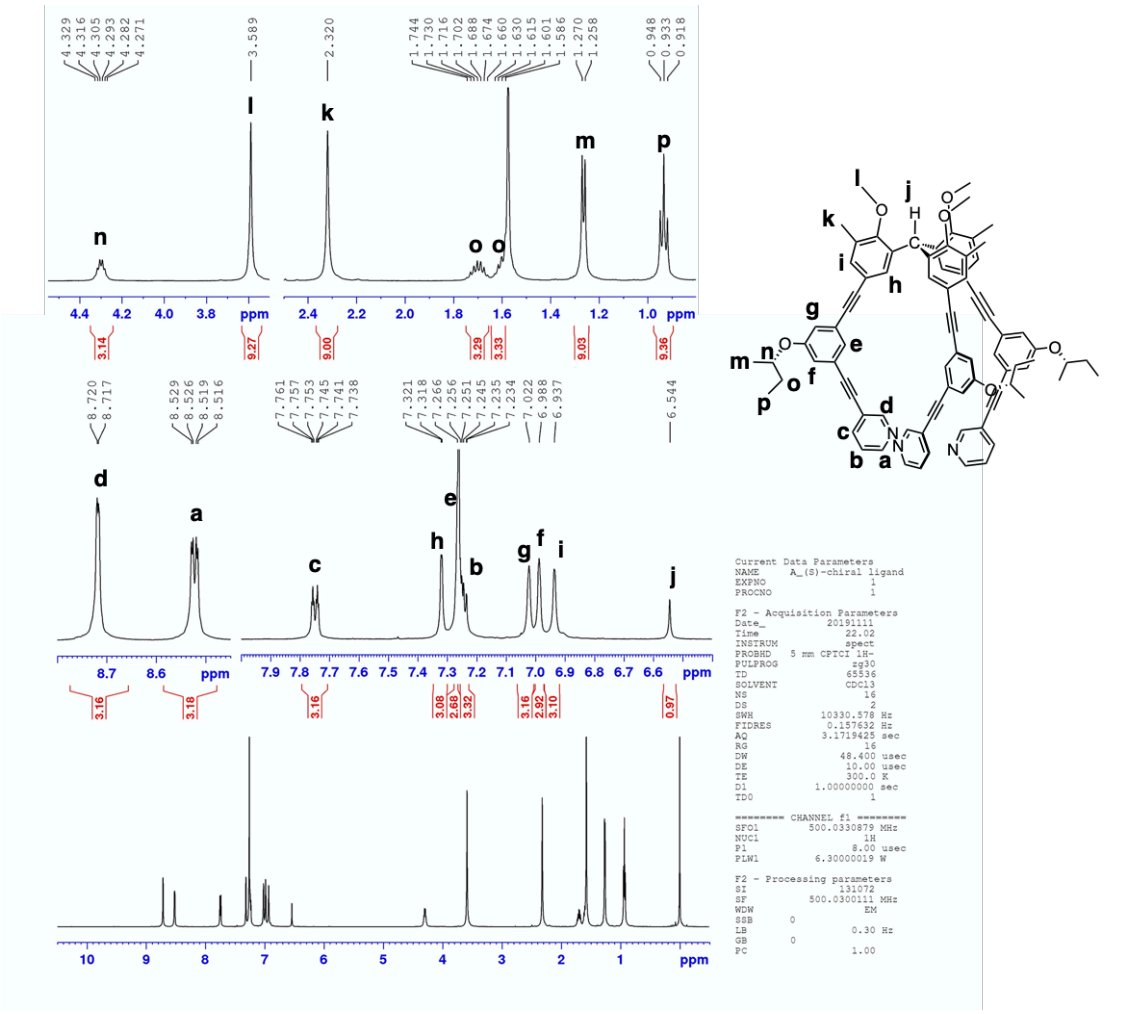

Figure S43. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **(*S*)-1b**.

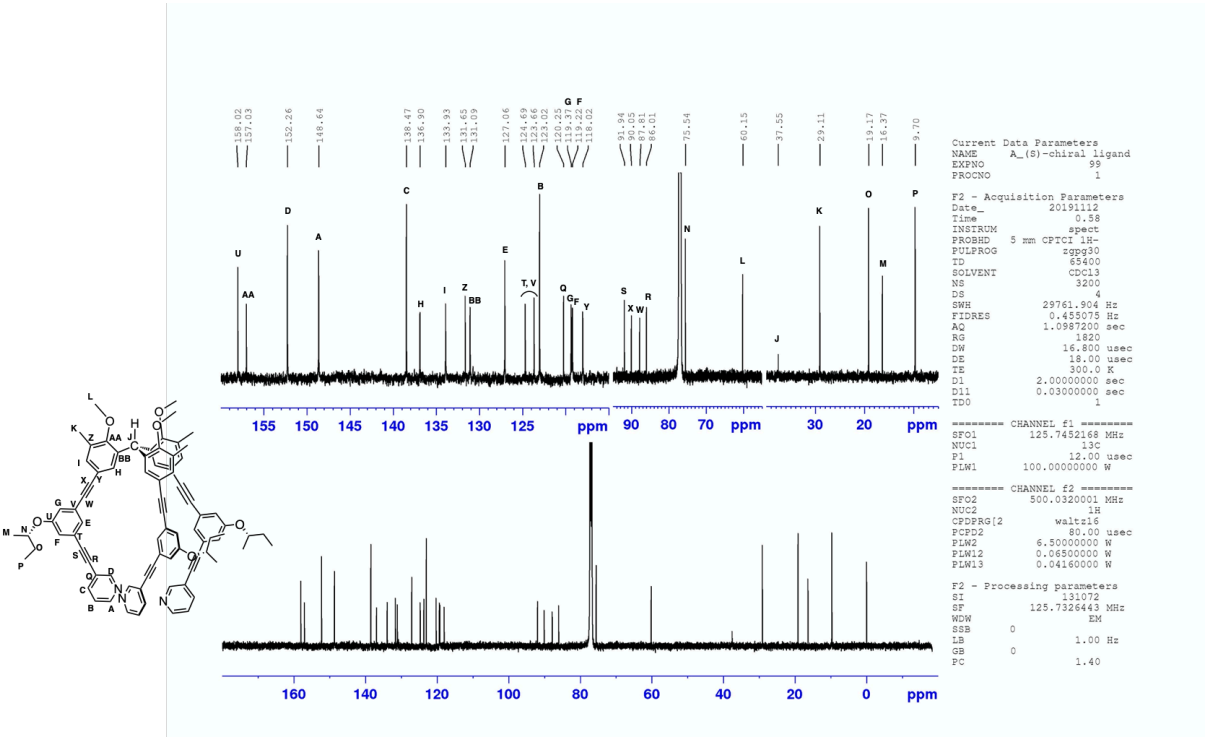

Figure S44. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **(*S*)-1b**.

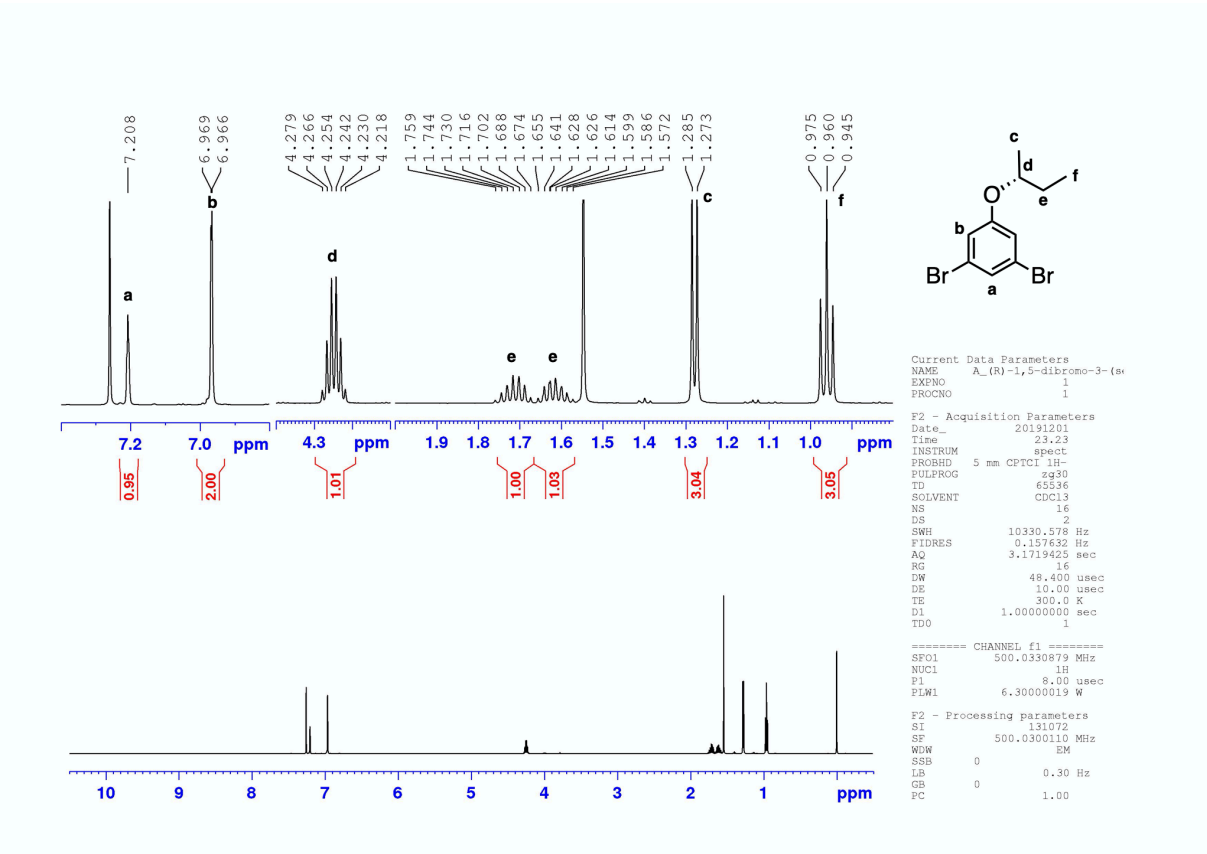

Figure S45. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **S6**.

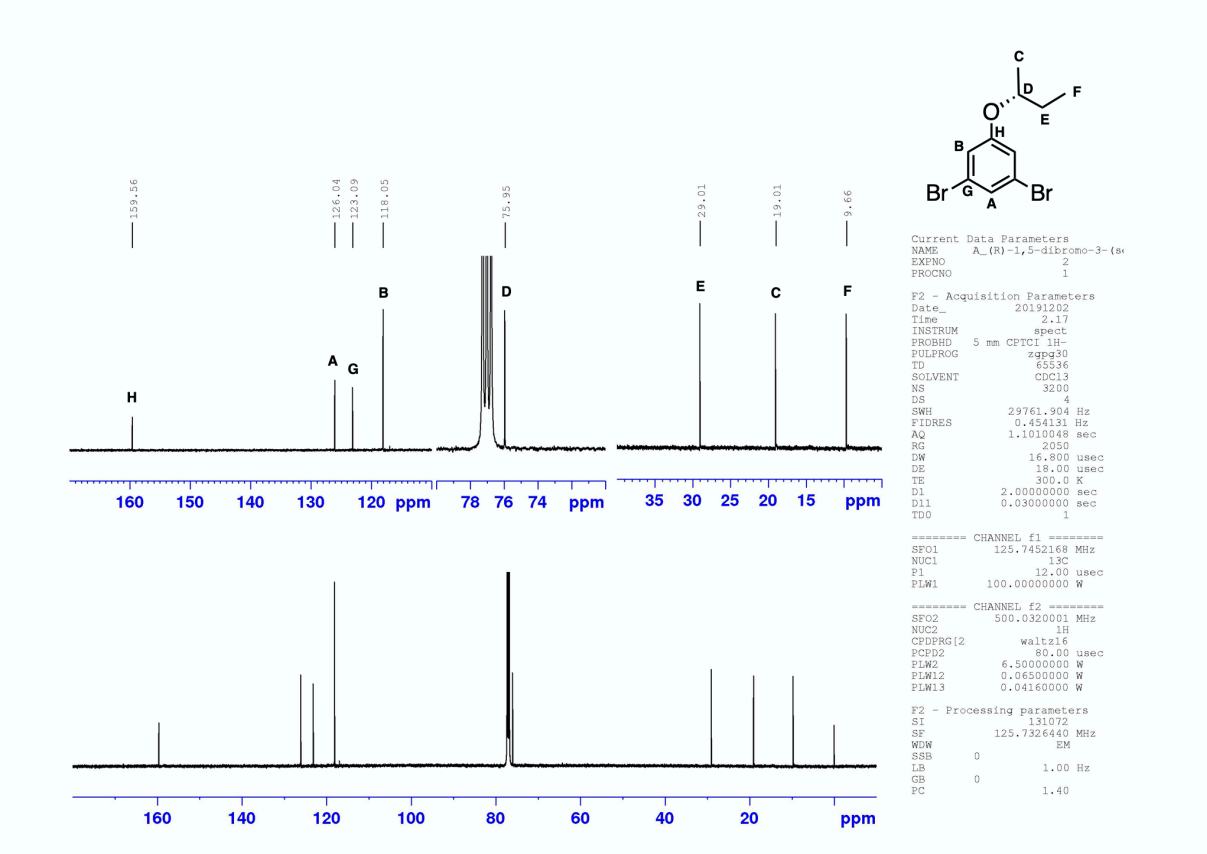

Figure S46. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **S6**.

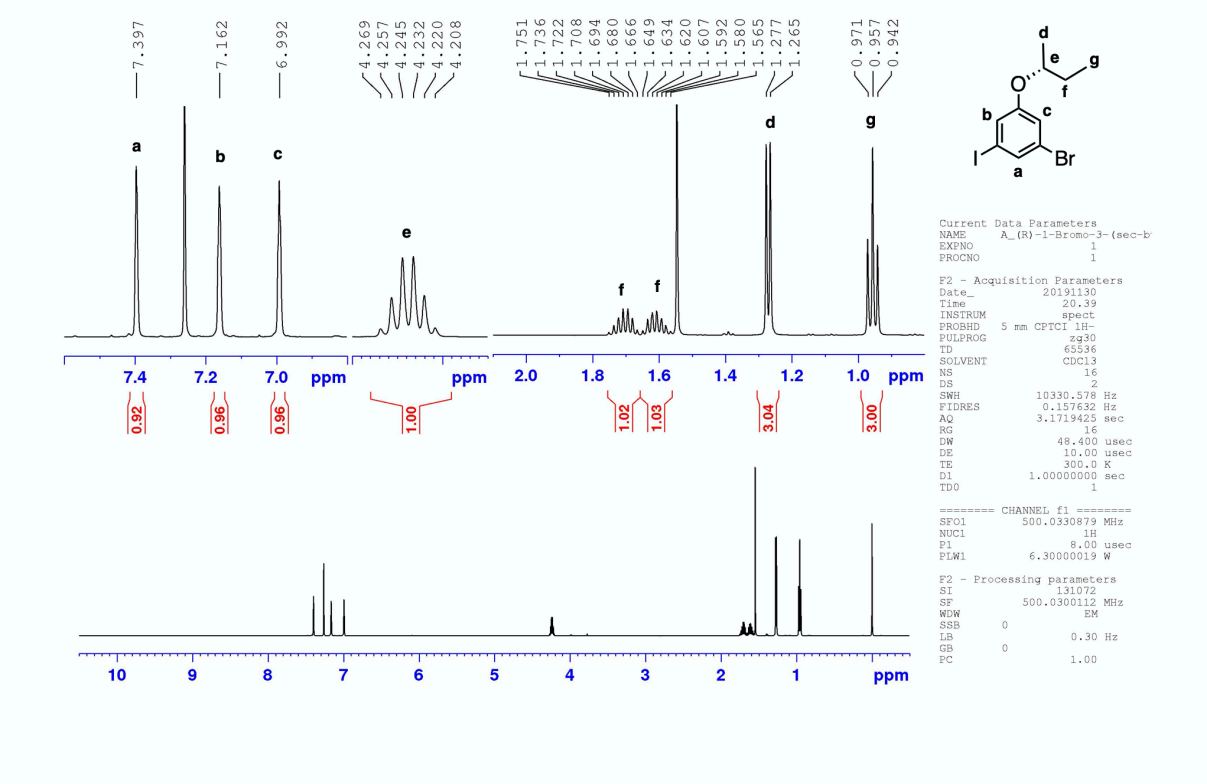

Figure S47. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **S7**.

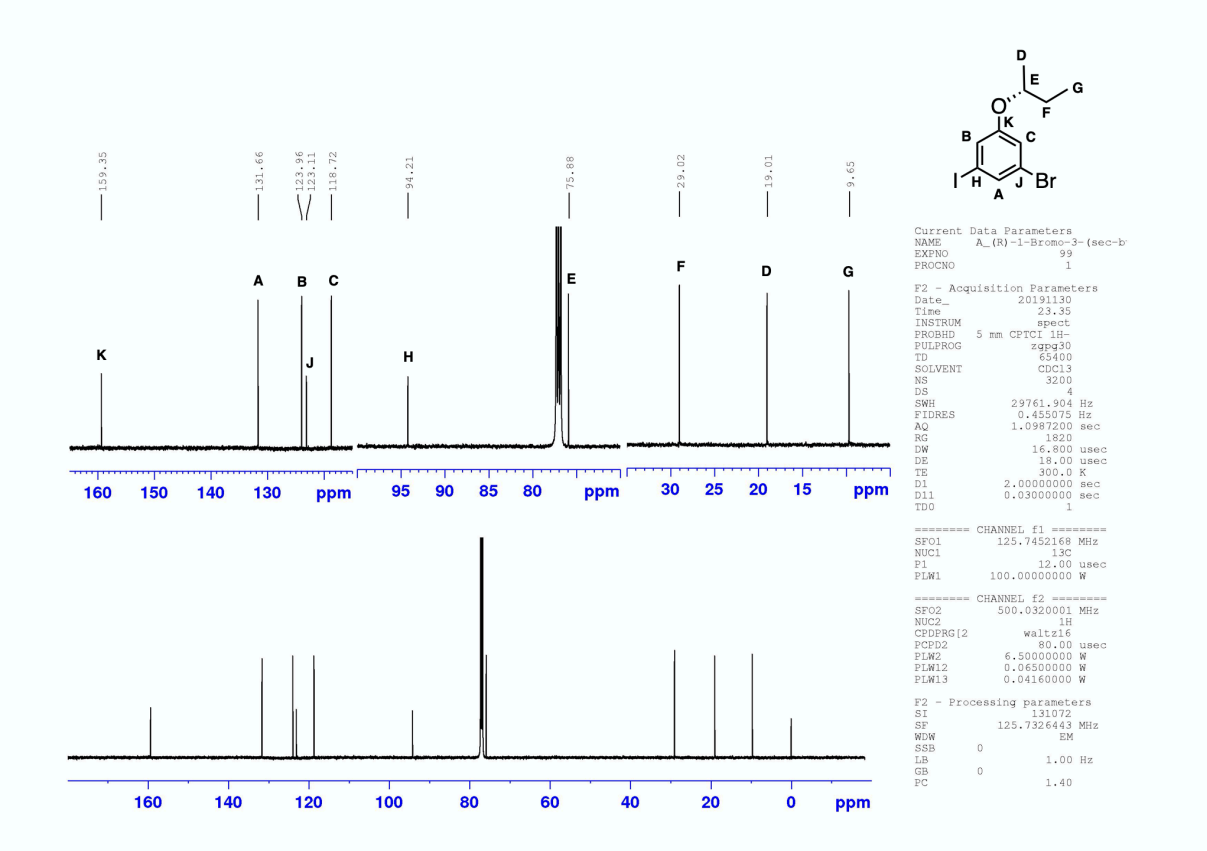

Figure S48. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **S7**.

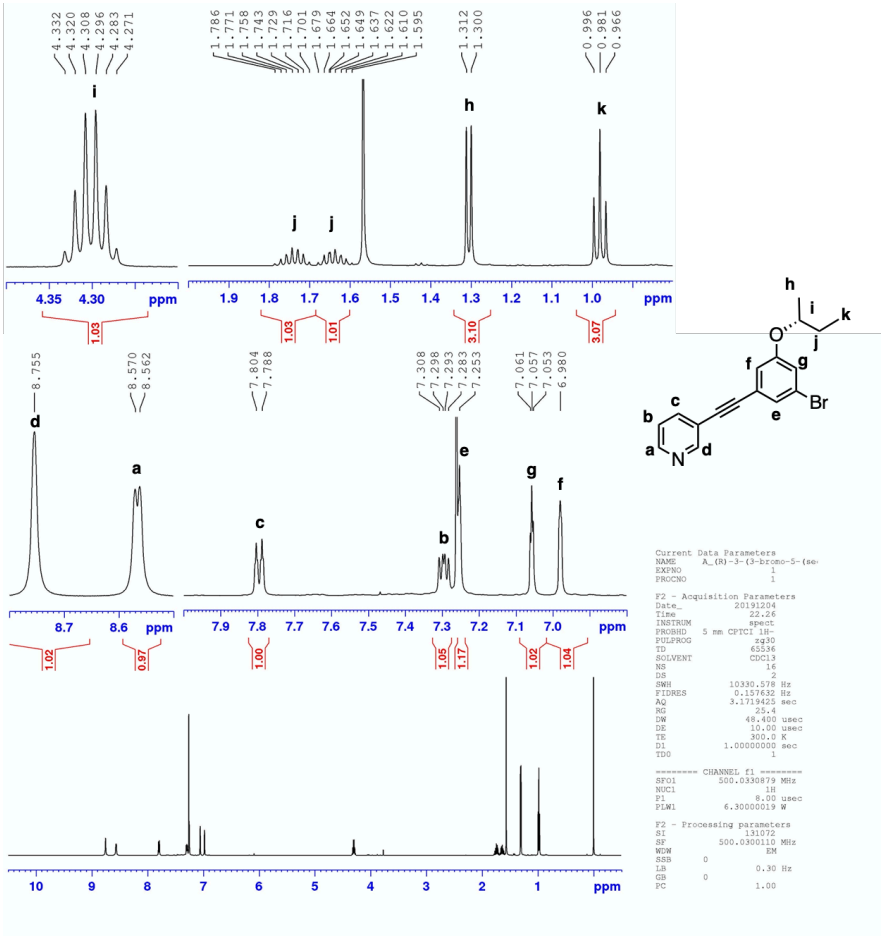

Figure S49. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **S8**.

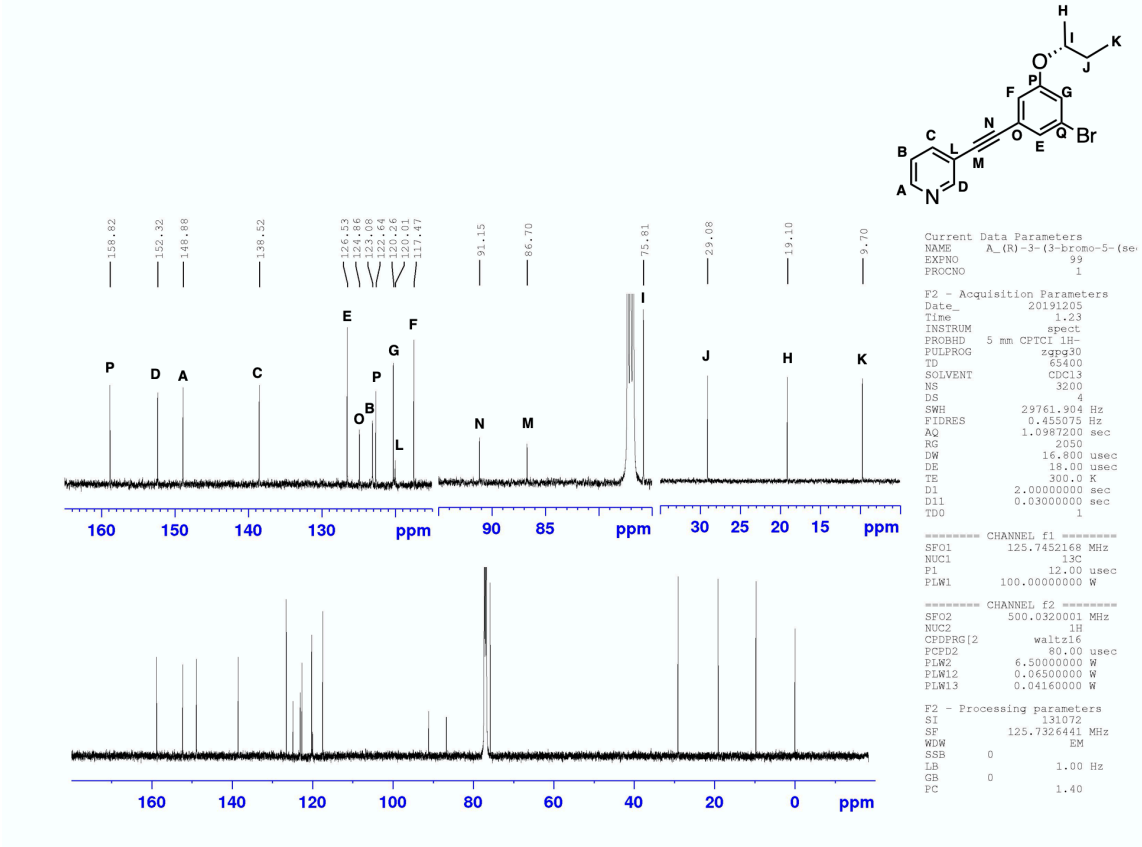

Figure S50. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **S8**.

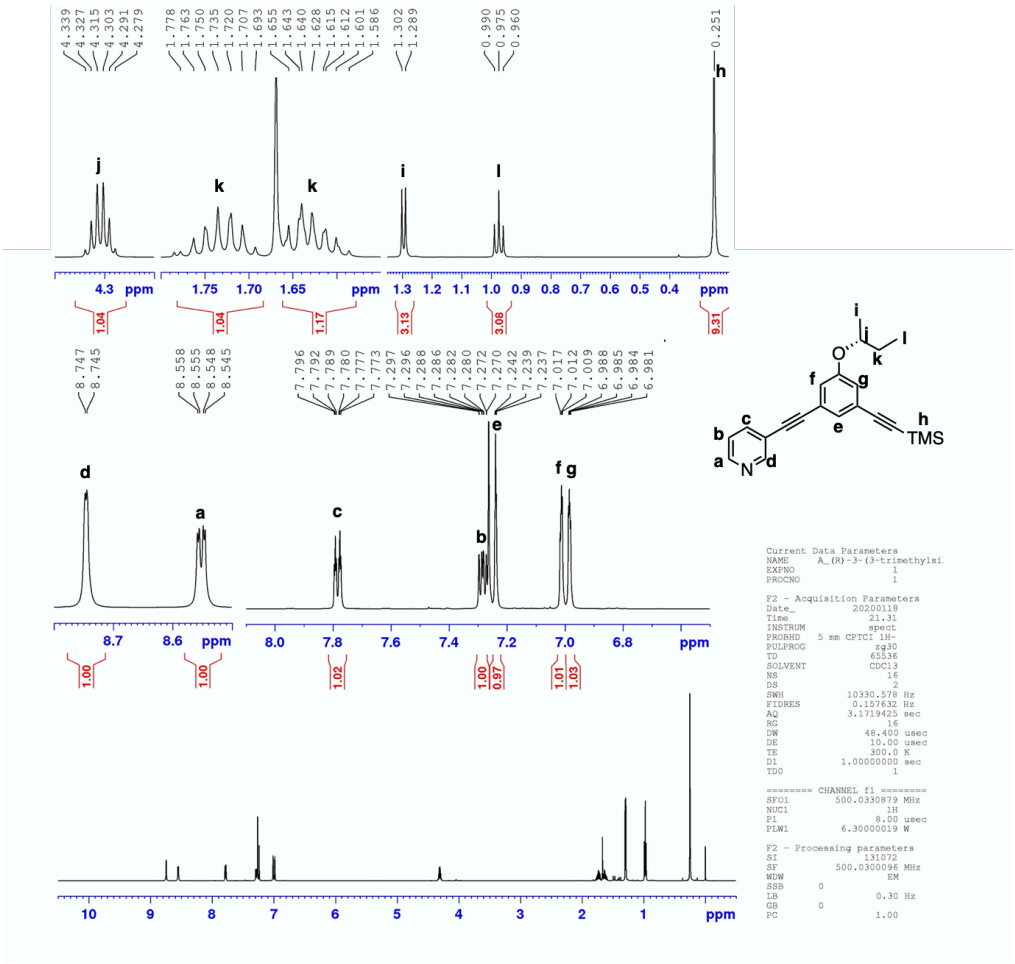

Figure S51. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **S9**.

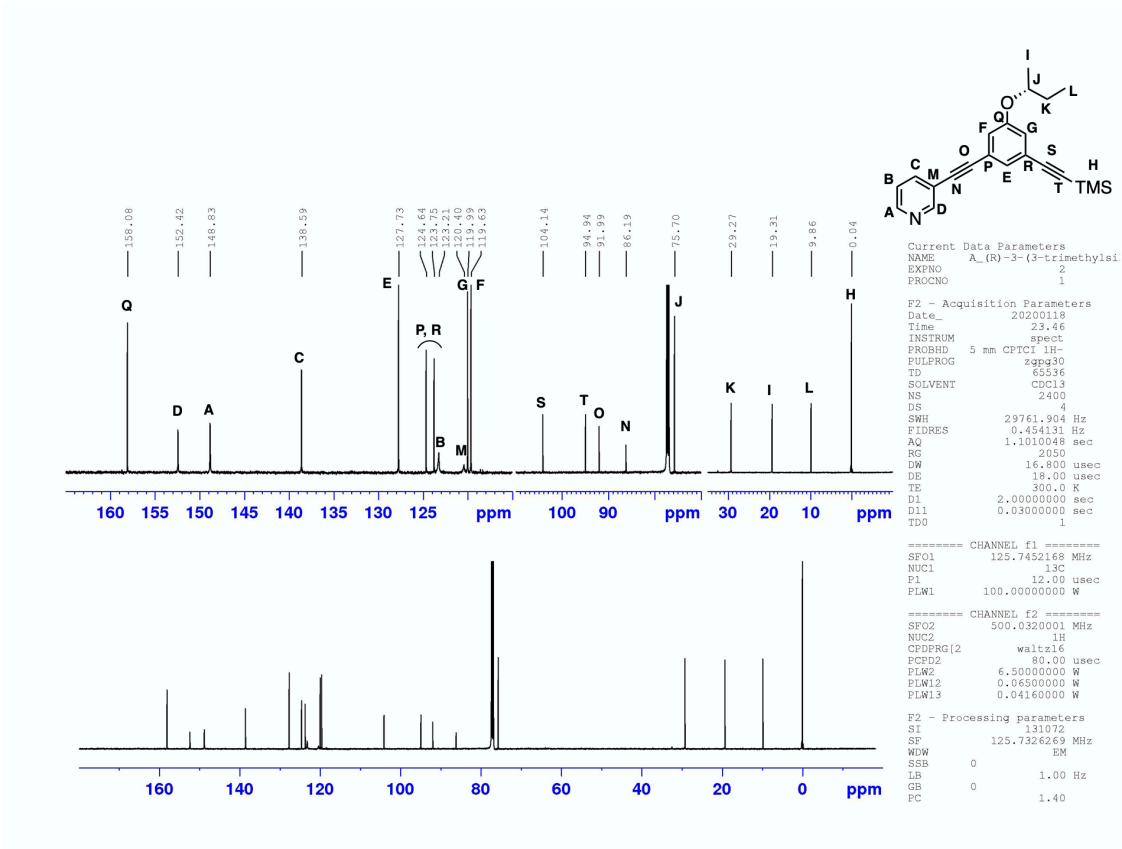

Figure S52. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **S9**.

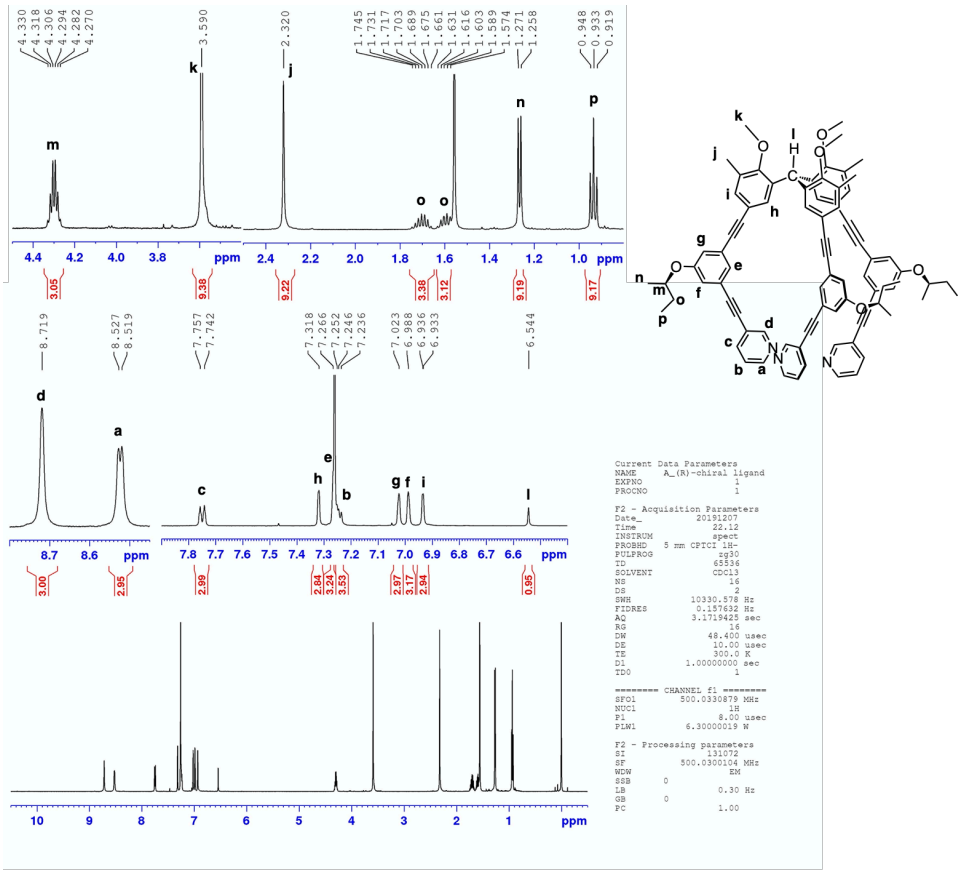

Figure S53. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **(*R*)-1b**.

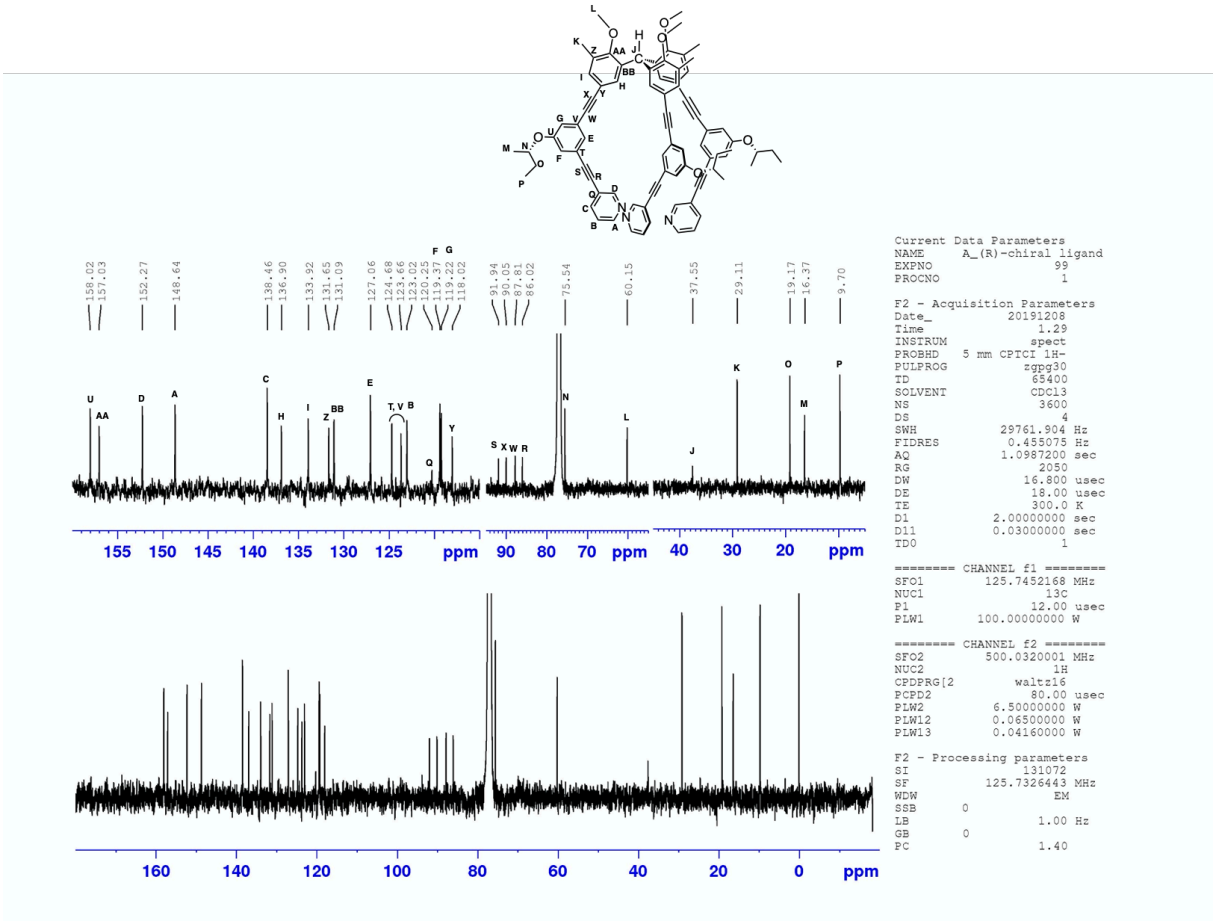

Figure S54. ^{13}C NMR (126 MHz, $CDCl_3$, 300 K) spectrum of **(*R*)-1b**.

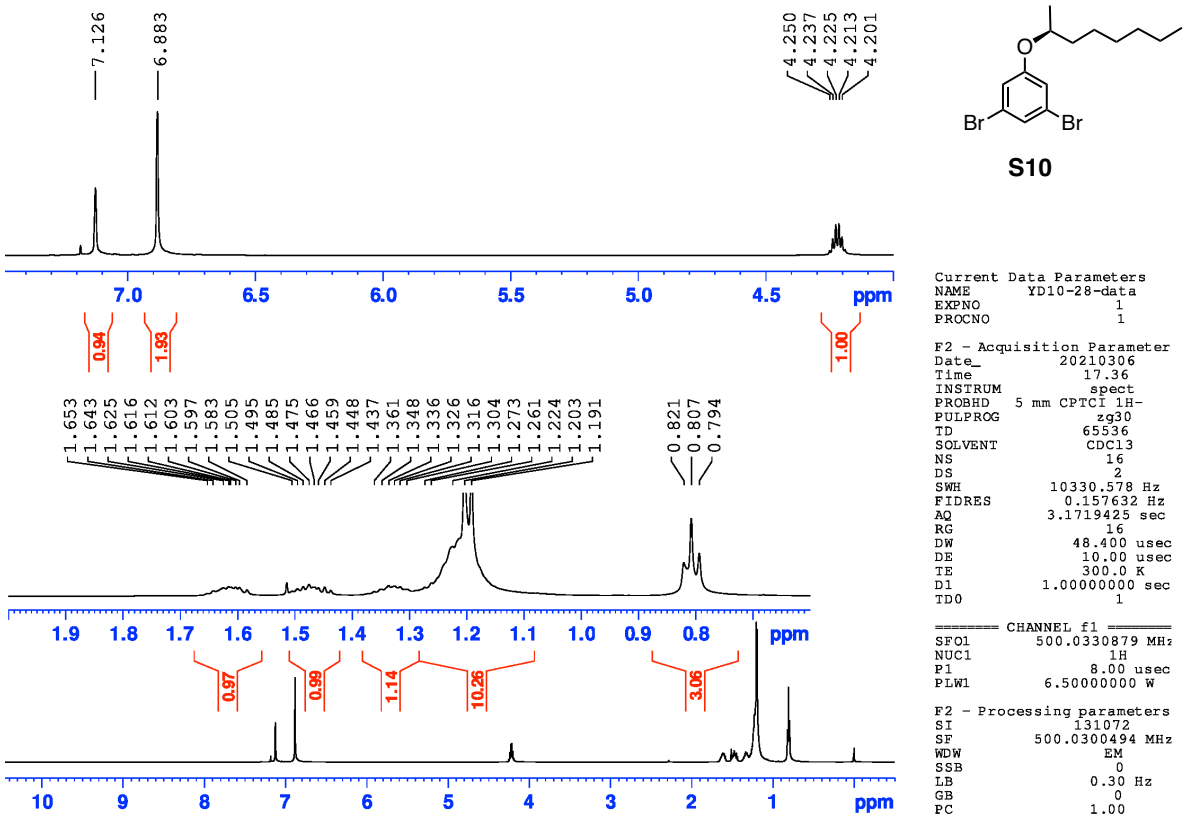

Figure S55. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **S10**.

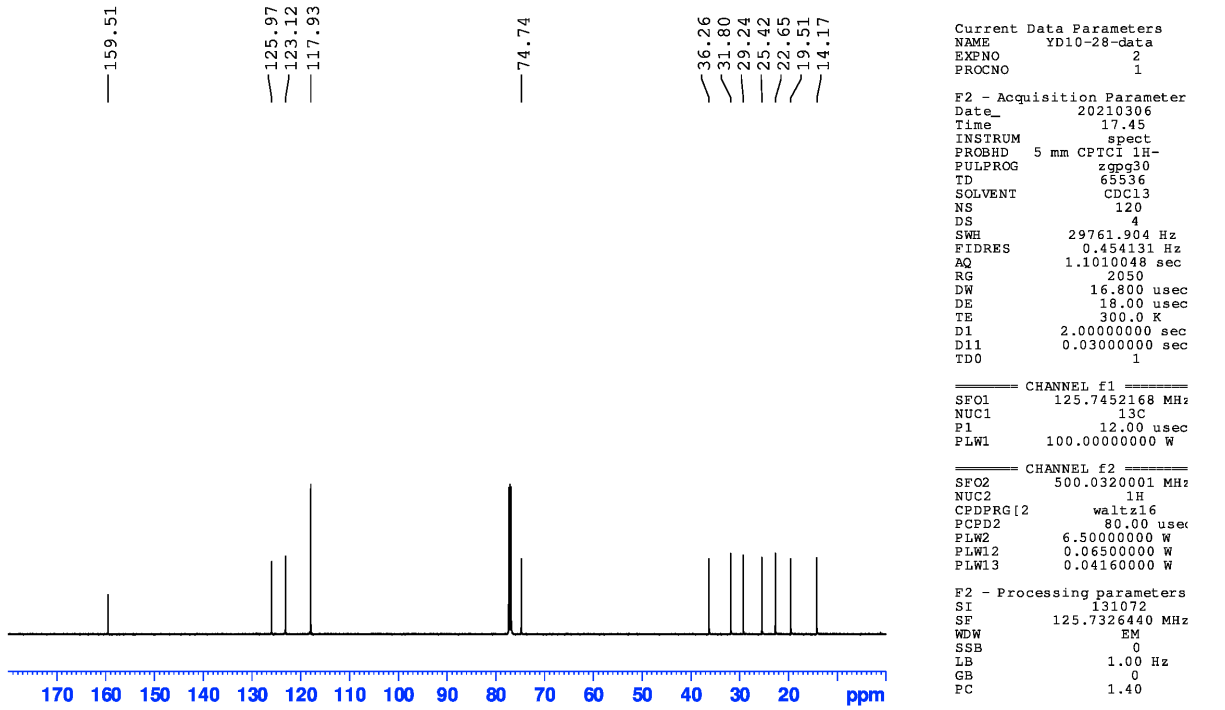

Figure S56. ^{13}C NMR (126 MHz, $CDCl_3$, 287 K) spectrum of **S10**.

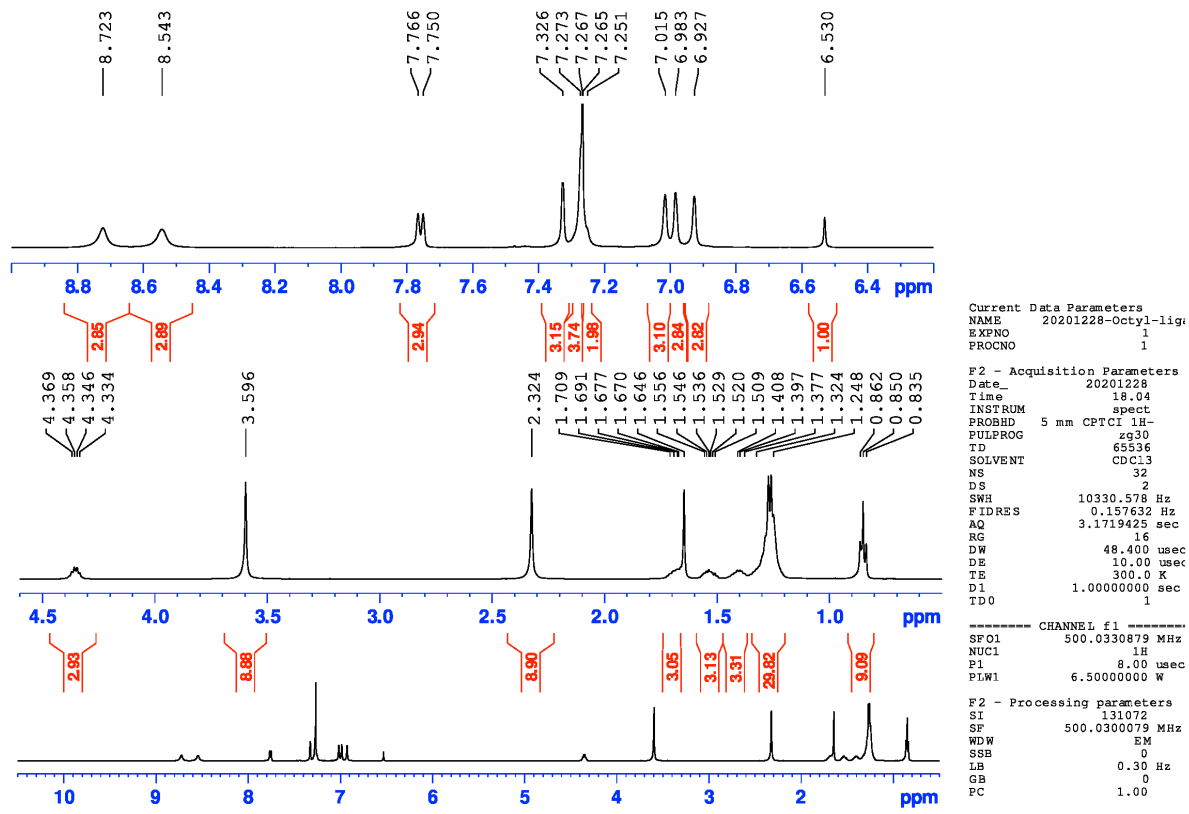

Figure S57. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **(*S*)-1c**.

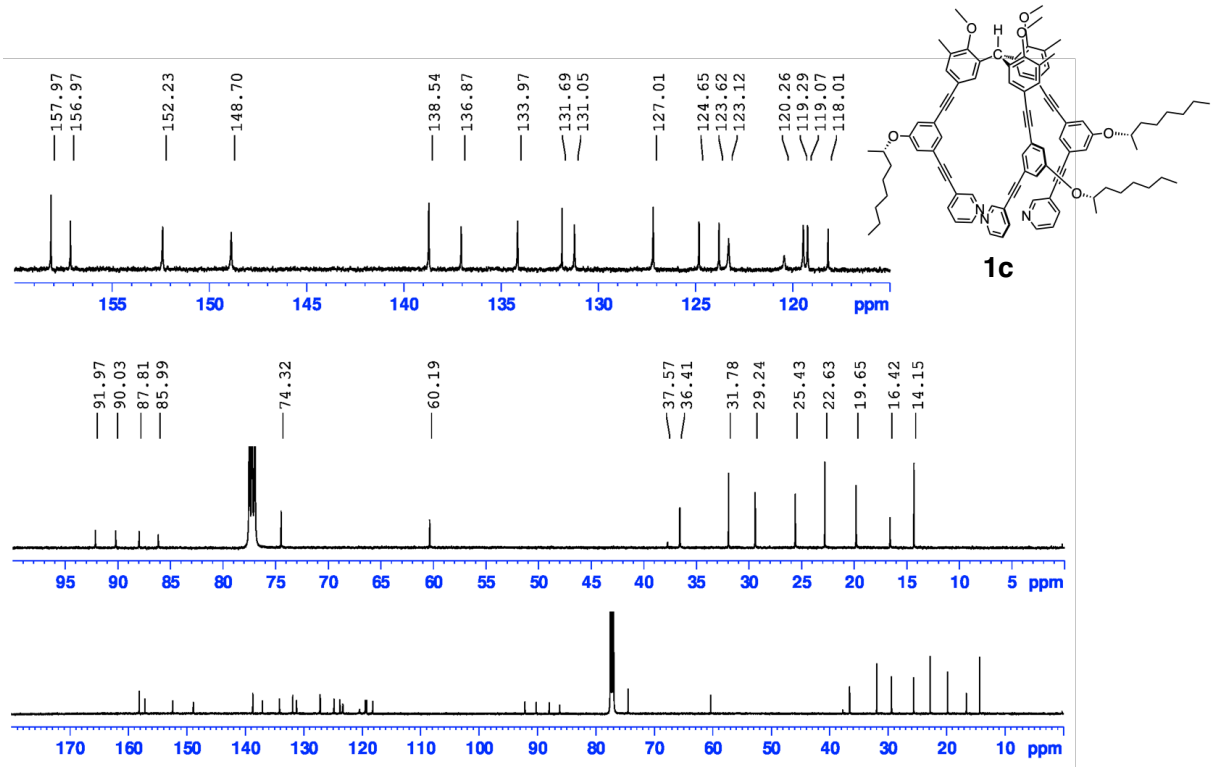

Figure S58. ^{13}C NMR (126 MHz, $CDCl_3$, 287 K) spectrum of **(*S*)-1c**.

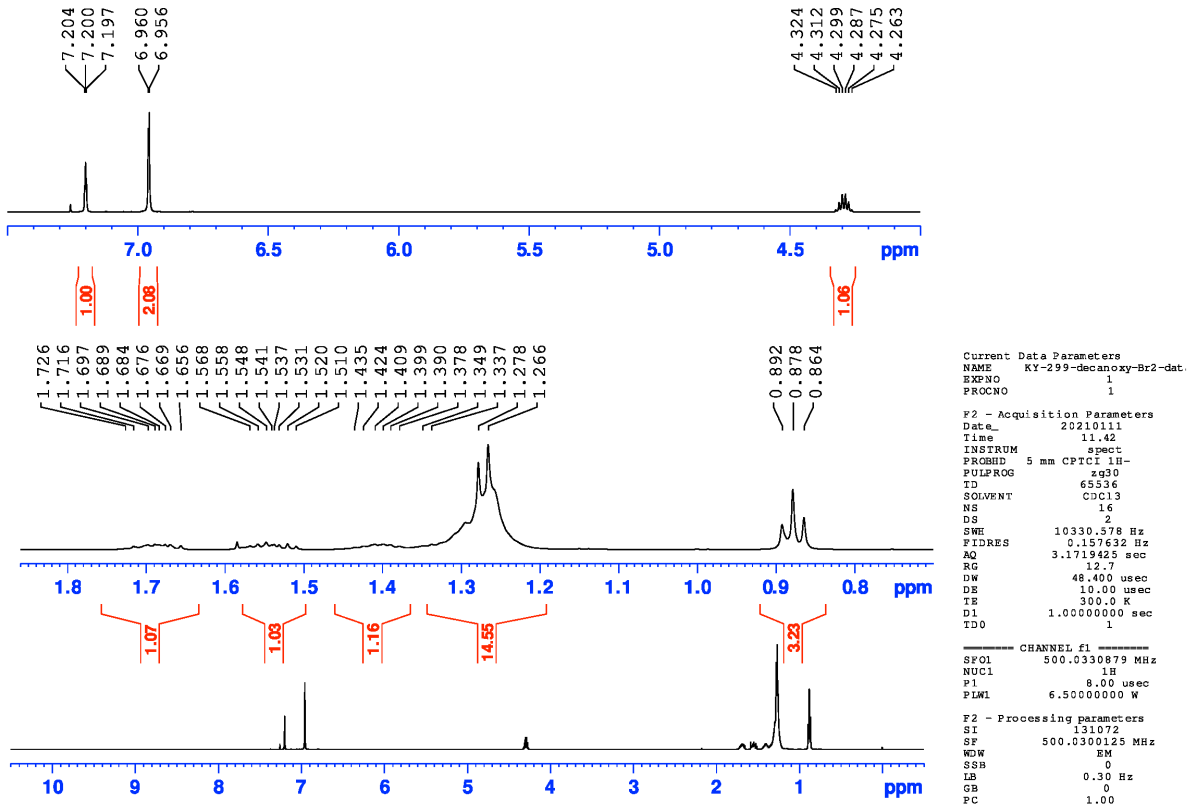

Figure S59. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **S12**.

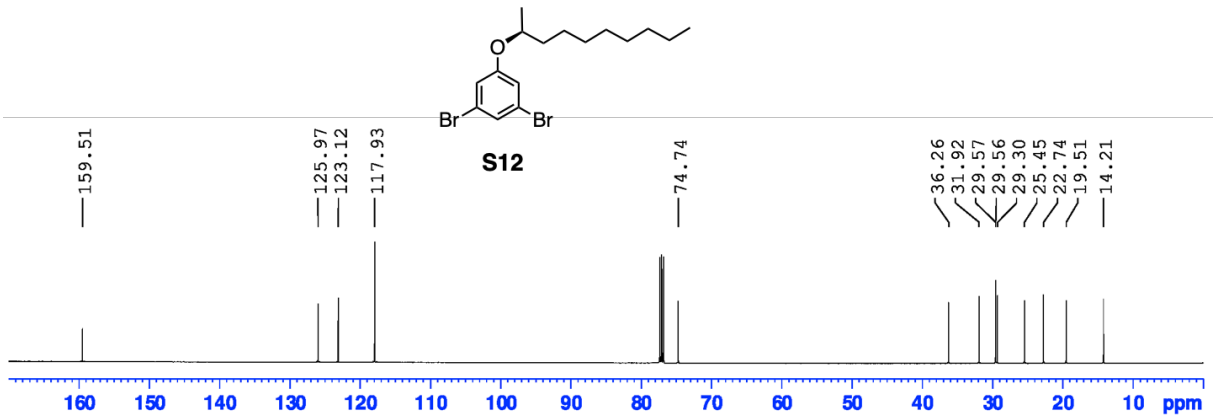

Figure S60. ^{13}C NMR (126 MHz, $CDCl_3$, 287 K) spectrum of **S12**.

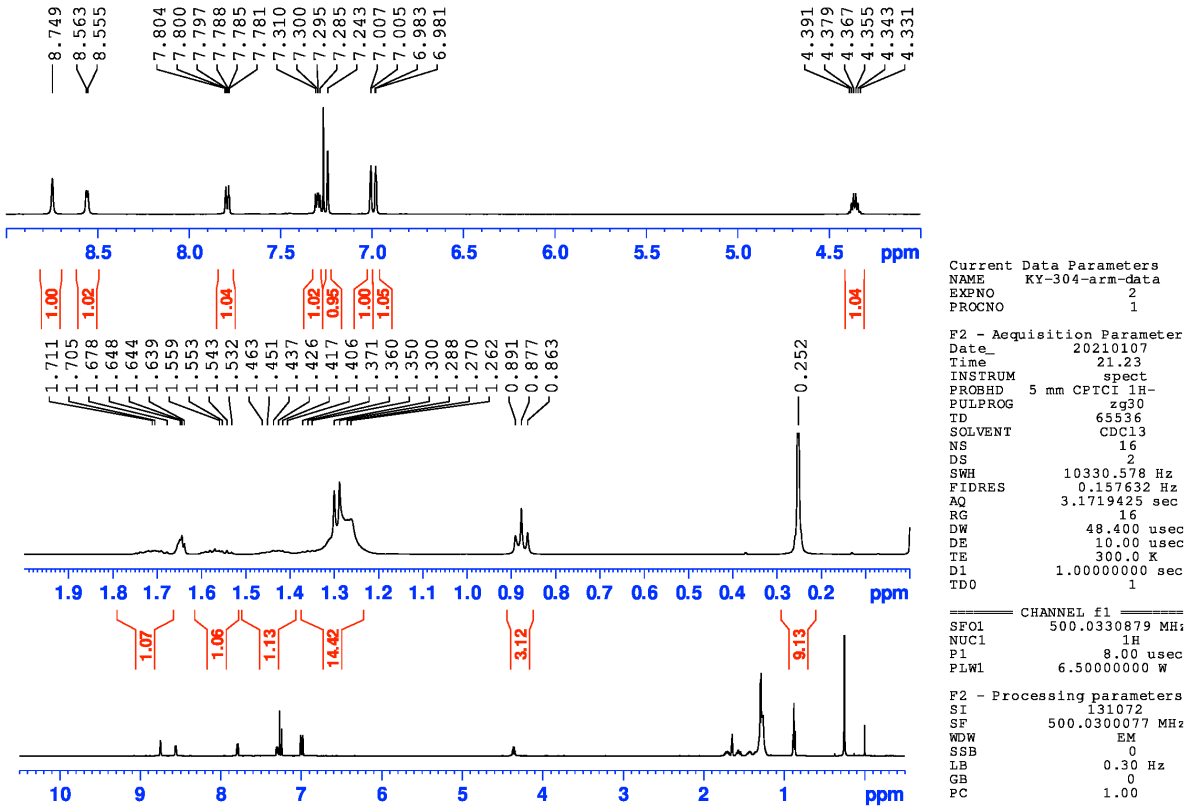

Figure S61. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **S13**.

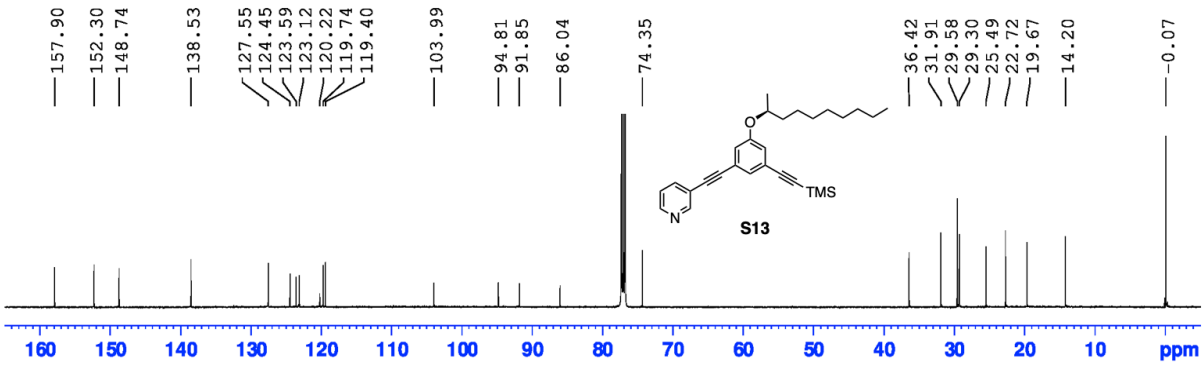

Figure S62. ^{13}C NMR (126 MHz, $CDCl_3$, 287 K) spectrum of **S13**.

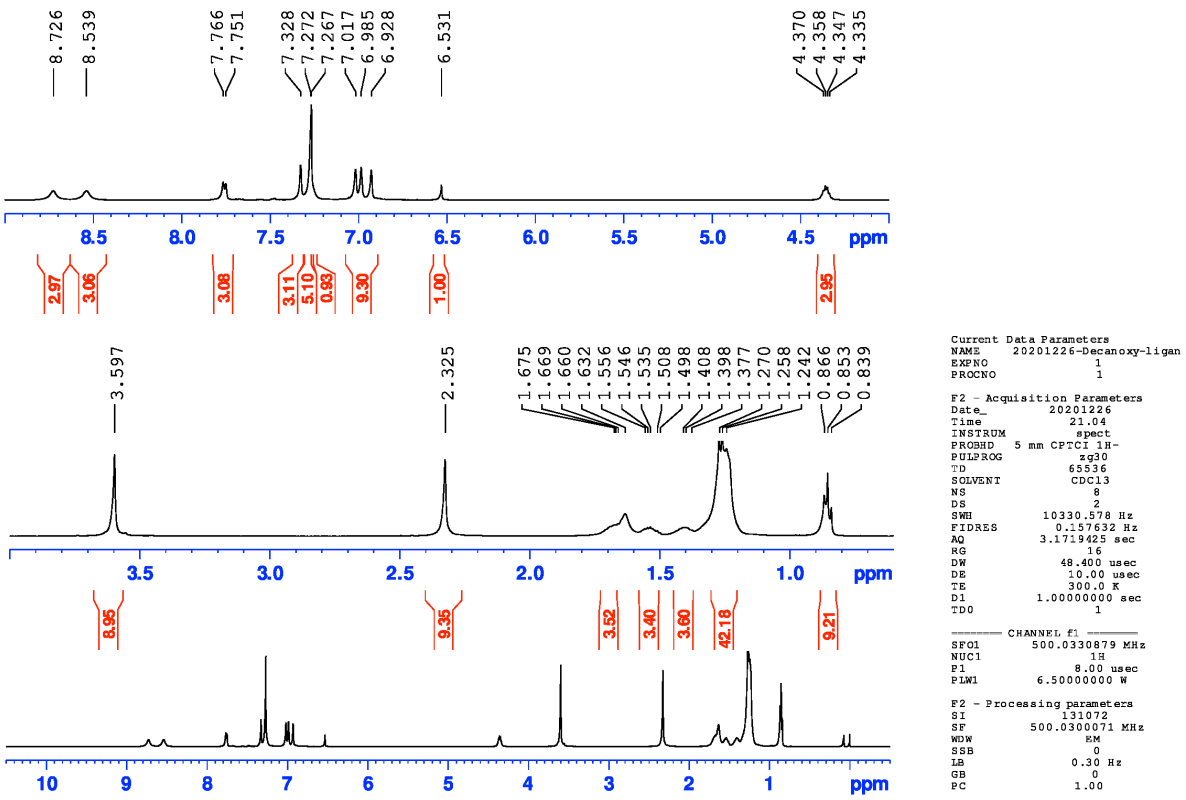

Figure S63. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **(*S*)-1d**.

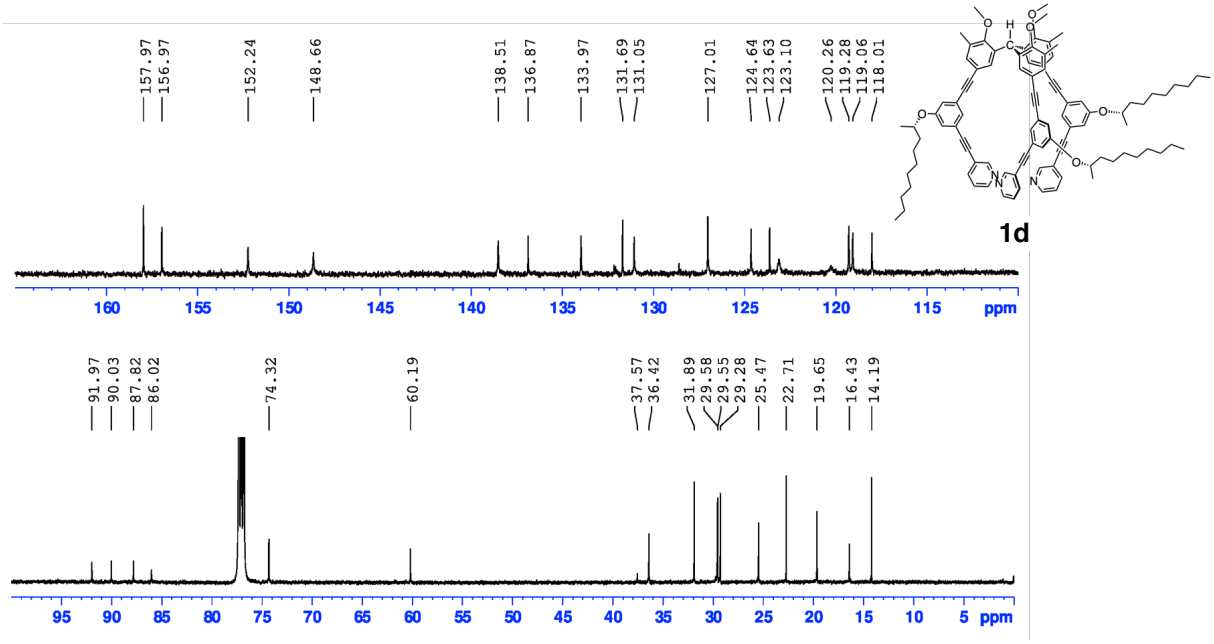

Figure S64. ^{13}C NMR (126 MHz, $CDCl_3$, 287 K) spectrum of **(*S*)-1d**.

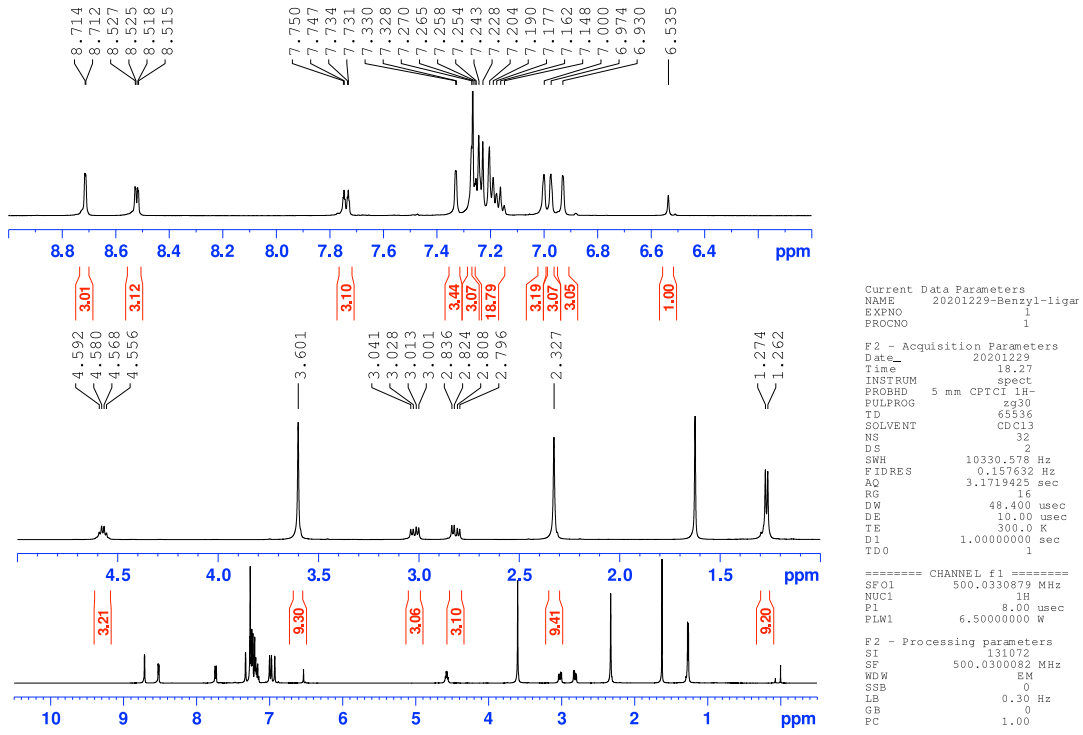

Figure S65. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of **(*S*)-1e**.

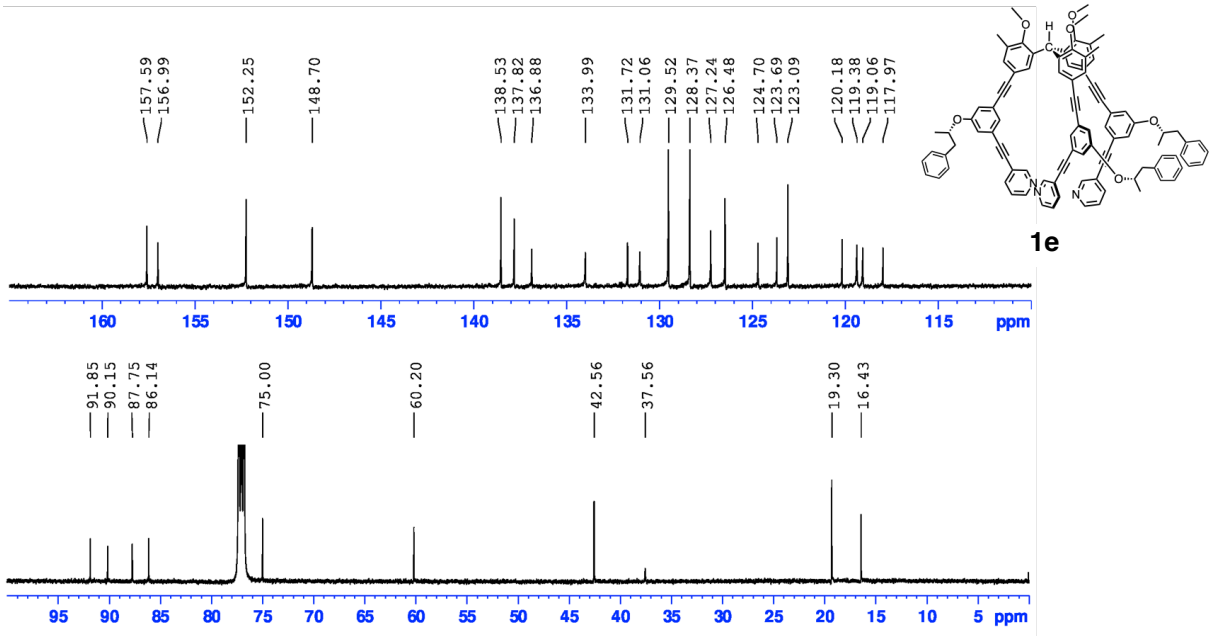

Figure S66. ^{13}C NMR (126 MHz, $CDCl_3$, 287 K) spectrum of **(*S*)-1e**.