Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary Information

Synthesis and Chiroptical Properties of Cylindrical Macrocycles Comprising Two Calix[3]aramide Moieties

Yuuki Saito,[a] Misa Satake,[a] Ryuichi Mori,[a] Misaki Okayasu,[a] Hyuma Masu,[b] Masahide Tominaga,[c] Kosuke Katagiri,[d] Kentaro Yamaguchi,[c] Shoko Kikkawa,[a] Hidemasa Hikawa[a] and Isao Azumaya*[a]

[a]Faculty of Pharmaceutical Sciences, Toho University, 2-2-1 Miyama, Funabashi, Chiba 274-8510, Japan.

[b]Center for Analytical Instrumentation, Chiba University, 1-33 Yayoi-cho, Inage-ku, Chiba 263-8522, Japan.

[c]Faculty of Pharmaceutical Sciences at Kagawa Campus, Tokushima Bunri University, 1314-1 Shido, Sanuki, Kagawa 769-2193, Japan.

[d]Department of Chemistry, Faculty of Science and Engineering, Konan University, 8-9-1 Okamoto, Higashinada-ku, Kobe, Hyogo 658-8501, Japan.

E-mail: isao.azumaya@phar.toho-u.ac.jp
Fax: +81-47-472-1585
Tel: +81-47-472-1589

Table of Contents

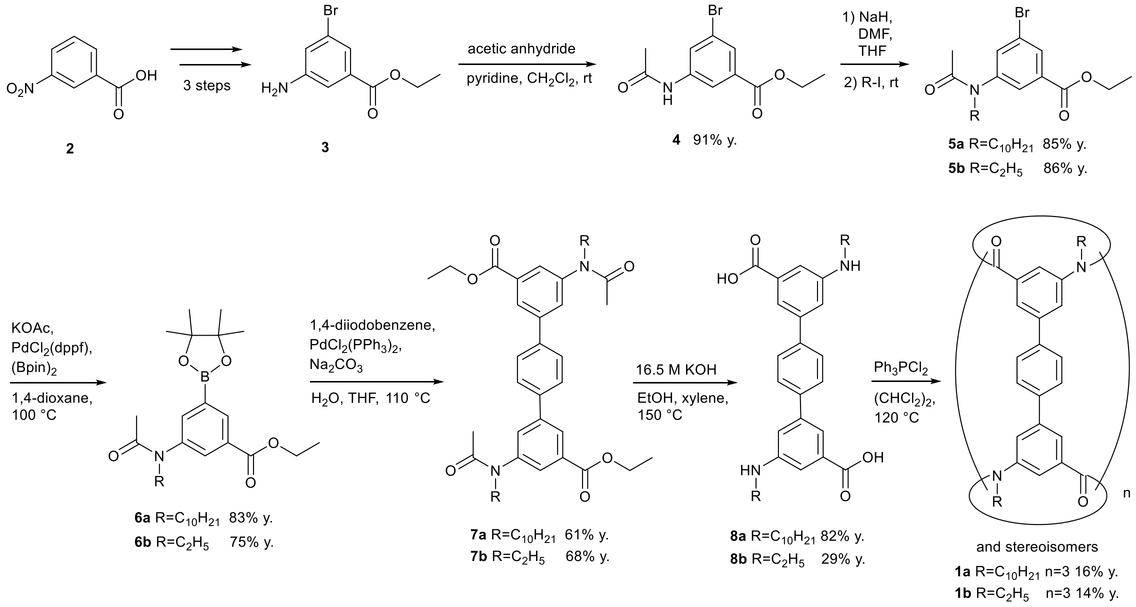
Abbreviation: DMF = *N*,*N*-dimethylformamide, THF = tetrahydrofuran, $(Bpin)_2$ = bis(pinacolato)diboron, dppf = 1,1'-bis(diphenylphosphino)ferrocene, rt = room temperature

1. General experimental

All of starting materials and solvents were purchased from Alfa Aesar, KANTO CHEMICAL CO., INC., TCI, Wako. Ethyl 3-amino-5-bromobenzoate was synthesized following to the known procedure.[S1] ^{1}H and ^{13}C NMR spectra, ^{1}H–^{1}H correlation spectroscopy (COSY), ^{1}H–^{13}C heteronuclear single-quantum correlation spectroscopy (HSQC), ^{1}H–^{13}C heteronuclear multiple bond coherence (HMBC) and 1D nuclear Overhauser effect (1D-NOE) were recorded on JEOL JNM-ECS400 spectrometer (400 MHz for ^{1}H, 100 MHz for ^{13}C), and the internal standards of ^{1}H and ^{13}C NMR spectra were tetramethylsilane (0.00 ppm) and solvent residual peaks. The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, dd = double doublet, m = multiplet, brs = broad singlet. Infrared (IR) spectra were recorded on a JASCO FT-IR-4100 spectrophotometer. Electron ionization mass spectra (EI-MS) and Fast atom bombardment mass spectra (FAB-MS) were performed on a JEOL JMS700 MStation mass system. Column chromatography was performed on silica gel (Silica gel PSQ 100B, spherical, 3–100 nm, Fuji Silysia) with a specified solvent. Purifications with preparative gel permeation chromatography (GPC) were carried out on a Japan analytical industry LC-9210II NEXT system using tandem JAIGEL 2HH columns ($CHCl_3$ as an eluent, flow rate = 5.0 mL/min) equipped with an ultraviolet (UV) detector monitored at 254 nm. The chiral high performance liquid chromatography (HPLC) analysis was performed on a JASCO PU-2080 liquid chromatograph equipped with a UV detector (JASCO UV-2075) using a CHIRALPAK IA column (Daicel Chemical Industries, Ltd) (1.0 cm (i.d.) × 25 cm). UV-Vis spectra of $\sim 1.0 \times 10^{-5}$ M solutions in ethanol were recorded in 10 mm quartz cell on a HITACHI U-3010 spectrophotometer equipped. Fluorescence spectra of $\sim 1.0 \times 10^{-7}$ M solutions in ethanol were recorded in 10 mm quartz cell on JASCO FP-6200 spectrofluorometer. The electronic circular dichroism (ECD) spectra of $\sim 1.0 \times 10^{-5}$ M solutions in ethanol were measured in 10 mm quartz cells on a JASCO J-1500 spectrophotometer. The temperature was controlled with a liquid nitrogen-controlled 10 mm quartz cell in a cryostat from +20 °C to −90 °C. The vibrational CD (VCD) spectra were recorded with a spectrometer JASCO FVS-6000, using a 150 μm BaF_2 cell. The absorption signals were detected using an MCT infrared detector. The spectra of $\sim 1.2 \times 10^{-2}$ M solutions in $CDCl_3$ were collected for ca. 1 h with 4 cm^{-1} resolution. Signals were accumulated for 6000 scans. The circularly polarized luminescence (CPL) spectra of $\sim 1.0 \times 10^{-5}$ M solutions in ethanol were obtained at rt using a JASCO CPL-300 spectrofluorometer. Signals were accumulated for 25 scans.

2. Synthesis

Cylindrical macrocycles 1a and 1b



Ethyl 3-acetamido-5-bromobenzoate (4).

A solution of ethyl 3-amino-5-bromobenzoate (**3**) (23 g, 93 mmol), acetic anhydride (45 mL, 0.48 mol, 5.0 eq.) and dehydrated pyridine (38 mL, 0.48 mol, 5.0 eq.) in dehydrated dichloromethane (980 mL) was stirred at room temperature for 1.5 h under argon atmosphere. The reaction mixture was poured into water, and extracted with dichloromethane. The organic layer was washed with twice 2 M HCl, brine, sat. $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by trituration using *n*-hexane to give product **4** as a white solid (24 g, 85 mmol, 91%). M.p. 157–159 °C. FT-IR (KBr): 3449, 1718, 1668 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (t, 3H, *J* = 7.2 Hz), 2.20 (s, 3H), 4.37 (q, 2H, *J* = 7.2 Hz), 7.29 (s, 1H), 7.84 (t, 1H, *J* = 1.6 Hz), 7.90 (t, 1H, *J* = 1.6 Hz), 8.20 (t, 1H, *J* = 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 24.7, 61.7, 119.2, 122.9, 126.9, 128.1, 132.6, 139.3, 165.1, 168.7; LRMS (EI) *m/z* = 285 [M$^+$]. Anal. Calcd for $C_{11}H_{12}BrNO_3$: C, 46.18; H, 4.23; N, 4.90. found: C, 46.01; H, 4.31; N, 4.93.

Ethyl 3-bromo-5-(*N*-decylacetamido)benzoate (5a).

To a solution of compound **4** (8.4 g, 29 mmol) dissolved in dehydrated DMF (120 mL) and dehydrated THF (30 mL) under argon atmosphere, we added sodium hydride (1.4 g, 55% purity, 32 mmol, 1.1 eq.). To the solution of **4** stirred at 0 °C for 15 minutes, 1-iododecane (7.1 mL, 33 mmol, 1.1 eq.) was added and stirred at room temperature for overnight. The reaction mixture was poured into water, and extracted with ethyl acetate. The organic layer was washed with 2 M HCl, brine, sat. $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography (*n*-hexane : ethyl acetate = 5:1) to give **5a** as a yellow oil (11 g, 25 mmol, 85%). FT-IR (KBr): 2925, 2854, 1725, 1670 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, 3H, *J* = 7.2 Hz), 1.18–1.32 (m, 14H), 1.41 (t, 3H, *J* = 7.2 Hz), 1.44–1.53 (m, 2H), 1.85 (s, 3H), 3.67 (t, 2H, *J* = 7.6 Hz), 4.40 (q, 2H, *J* = 7.2 Hz), 7.51 (t, 1H, *J* = 2.0 Hz), 7.77 (t, 1H, *J* = 1.6 Hz), 8.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ14.2, 14.4, 22.8, 23.0, 26.8, 27.8, 29.4, 29.6, 29.6 32.0, 49.3, 62.0, 123.0, 128.1, 132.0, 133.7, 135.4, 144.7, 164.5, 169.7; HRMS (EI) calcd for $C_{21}H_{32}{}^{79}BrNO_3$ [M^+]: 425.1557, found 425.1566.

Ethyl 3-bromo-5-(*N*-ethylacetamido)benzoate (5b).

Sodium hydride (0.44 g, 55% purity, 11 mmol, 1.1 eq.) was washed with *n*-hexane twice, which was suspended in dehydrated DMF (10 mL). The compound **4** (2.8 g, 10 mmol) was dissolved in dehydrated DMF (30 mL) and dehydrated THF (10 mL) under argon atmosphere. After the suspension was added to the solution of **4**, 1-iodoethane (0.9 mL, 11 mmol, 1.1 eq,) was added to the mixture and stirred at room temperature for overnight. The reaction mixture was poured into water, and extracted with ethyl acetate. The organic layer was washed with 2 M HCl, brine, sat. $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography (*n*-hexane : ethyl acetate = 4:1) to give **5b** as a yellow solid (2.7 g, 8.6 mmol, 86%). M.p. 55–57 °C. FT-IR (KBr): 2983, 1719, 1662 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.12 (t, 3H, *J* = 7.2 Hz), 1.41 (t, 3H, *J* = 7.2 Hz), 1.85 (s, 3H), 3.56 (q, 2H, *J* = 7.6 Hz), 4.41 (q, 2H, *J* = 7.2 Hz), 7.53 (t, 1H, *J* = 2.0 Hz), 7.78 (t, 1H, *J* = 1.6 Hz), 8.16 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.2, 14.3, 23.0, 44.1, 62.0, 123.0, 128.1, 132.1, 133.7, 135.5, 144.4, 169.5, 169.5; HRMS (FAB) calcd for $C_{13}H_{17}{}^{79}BrNO_3$ $[M+H]^+$: 314.0387, found 314.0370.

Ethyl 3-(*N*-decylacetamido)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (6a).

A mixture of the compound **5a** (2.1 g, 5.0 mmol), bis(pinacolato)diboron (1.5 g, 6.0 mmol, 1.2 eq.), potassium acetate (0.98 g, 10 mmol, 2.0 eq.) and $PdCl_2$(dppf) (82 mg, 0.10 mmol, 0.02 eq.) in dehydrated 1,4-dioxane (20 mL) was stirred at 100 °C for 3 h under argon atmosphere. After cooling, the reaction mixture was diluted with ethyl acetate, and filtered over Celite. To the filtrate, 1 M $CuSO_4$ (200 mL) was added and stirred at room temperature for overnight under air. The mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography (*n*-hexane : ethyl acetate = 3:1) to give **6a** as a yellow oil (2.0 g, 4.1 mmol, 83%). FT-IR (KBr): 2926, 2855, 1723, 1669 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, 3H, *J* = 7.2 Hz), 1.19–1.31 (m,14H), 1.37 (s, 12H), 1.42 (t, 3H, *J* = 6.8 Hz), 1.45–1.52 (m, 2H), 1.81 (s, 3H), 3.69 (t, 2H, *J* = 7.6 Hz), 4.41 (q, 2H, *J* = 7.2 Hz), 7.75 (d, 1H, *J* = 1.2 Hz), 7.89 (t, 1H, *J* = 1.6 Hz), 8.41 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

14.2, 14.5, 22.8, 23.1, 25.0, 26.9, 27.8, 29.4, 29.6, 32.0, 49.2, 61.5, 84.6, 131.8, 131.9, 135.0, 138.4, 143.1, 165.9, 170.0; HRMS (EI) calcd for $C_{27}H_{44}BNO_5$ [M^+]: 473.3301, found 473.3324.

Ethyl 3-(*N*-ethylacetamido)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (6b).
A mixture of the compound **5b** (1.5 g, 5.0 mmol), bis(pinacolato)diboron (1.5 g, 6.0 mmol, 1.2 eq.), potassium acetate (0.98 g, 10 mmol, 2.0 eq.) and $PdCl_2$(dppf) (82 mg, 0.10 mmol, 0.02 eq.) in dehydrated 1,4-dioxane (25 mL) was stirred at 100 °C for 2 h under argon atmosphere. After cooling, the reaction mixture was diluted with ethyl acetate, and filtered over Celite. To the filtrate, 1 M $CuSO_4$ (200 mL) was added and stirred at room temperature for overnight under air. The mixture was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography (*n*-hexane : ethyl acetate = 3:1) to give **6b** as a white powder (1.3 g, 3.7 mmol, 75%). M.p. 64–66 °C. FT-IR (KBr): 2977, 1725, 1661 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (t, 3H, *J* = 7.2 Hz), 1.37 (s, 12H), 1.42 (t, 3H, *J* = 6.8 Hz), 1.82 (s, 3H), 3.77 (q, 2H, *J* = 7.2 Hz), 4.41 (q, 2H, *J* = 7.2 Hz), 7.76 (s, 1H), 7.90 (s, 1H), 8.42 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.2, 14.4, 23.0, 25.0, 44.0, 61.5, 84.6, 131.8, 132.0, 135.1, 138.5, 142.8, 165.8, 169.9; HRMS (FAB) calcd for $C_{19}H_{29}BNO_5$ [$M+H]^+$: 362.2131, found 362.2139.

Diethyl 5,5”-bis(*N*-decylacetamido)-[1,1’:4’,1”-terphenyl]-3,3”-dicarboxylate (7a).
A mixture of the compound **6a** (0.12 g, 0.25 mmol), 1,4-diiodobenzene (42 mg, 0.12 mmol, 0.5 eq.), sodium carbonate (0.72 g, 2.5 mmol, 10 eq.) and $PdCl_2(PPh_3)_2$ (19 mg, 28 μmol, 0.1 eq.) in THF (1.5 mL) and water (3 mL) was stirred at 110 °C for 2 h under argon atmosphere. After cooling, the reaction mixture was poured into water, and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography (toluene : ethyl acetate = 5:1) to give **7a** as a yellow solid (59 mg, 76 μmol, 61%). M.p. 114–116 °C. FT-IR (KBr): 2925, 1718, 1654 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (t, 6H, *J* = 7.2 Hz), 1.19–1.33 (m, 28H), 1.44 (t, 6H, *J* = 7.2 Hz), 1.51–1.58 (m, 4H), 1.91 (s, 6H), 3.75 (t, 4H, *J*=7.2 Hz), 4.45 (q, 4H, *J* = 7.2 Hz), 7.60 (s, 2H), 7.74 (s, 4H), 7.84 (s, 2H), 8.31 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 14.4, 22.8, 23.1, 26.9, 27.9, 29.4, 29.6, 29.6, 31.9, 49.3, 61.8 127.5, 127.9, 128.1, 130.9, 132.9, 139.0, 142.4, 144.2, 165.6, 169.9; MS (EI) *m/z*=768 [M^+]. Anal. calcd for $C_{48}H_{68}N_2O_6$: C, 74.96; H, 8.91; N, 3.64. found: C, 74.84; H, 8.65; N, 3.64.

Diethyl 5,5”-bis(*N*-ethylacetamido)-[1,1’:4’,1”-terphenyl]-3,3”-dicarboxylate (7b).
A mixture of the compound **6b** (1.8 g, 5.0 mmol), 1,4-diiodobenzene (0.82 g, 2.5 mmol, 0.5 eq.), sodium carbonate (14 g, 50 mmol, 10 eq.) and $PdCl_2(PPh_3)_2$ (0.35 g, 0.50 mmol, 0.1 eq.) in THF (35

mL) and water (35 mL) was stirred at 110 °C for 2 h under argon atmosphere. After cooling, the reaction mixture was poured into water, and extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography (chloroform : ethyl acetate = 3:1) to give **7b** as a yellow crystals (0.92 g, 1.7 mmol, 68%). M.p. 203–205 °C. FT-IR (KBr): 2979, 1725, 1661 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.18 (t, 6H, *J* = 7.2 Hz), 1.45 (t, 6H, *J* = 6.8 Hz), 1.92 (s, 6H), 3.84 (q, 4H, *J*=7.2 Hz), 4.45 (q, 4H, *J* = 7.2 Hz), 7.62 (s, 2H), 7.75 (s, 4H), 7.85 (s, 2H), 8.32 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.3, 14.4, 23.1, 44.1, 61.8 127.5, 127.9, 128.2, 131.0, 133.0, 139.0, 142.4, 143.9, 165.6, 169.8; HRMS (FAB) calcd for $C_{32}H_{37}N_2O_6$ $[M+H]^+$: 545.2642, found 545.2653.

5,5”-Bis(decylamino)-[1,1’:4’,1”-terphenyl]-3,3”-dicarboxylic acid (8a).

A solution of the compound **7a** (80 mg, 0.1 mmol) in xylene:ethanol (2:1, 1.5 mL) and 16.5 M KOH (0.5 mL) was stirred at 150 °C for 48 h. The reaction mixture was cooled in an ice-water bath and neutralized with 2 M HCl with cooling and subsequently extracted with chloroform. The organic layer was washed with water, and concentrated in vacuo. The residue was purified by trituration using *n*-hexane : ethyl acetate = 4:1 to give product **8a** as a white solid (54 mg, 80 μmol, 82%). M.p. 201–203 °C. FT-IR (KBr): 3420, 2925, 2848, 1682 cm^{-1}. ^1H NMR (400 MHz, DMSO-*d*$_6$) δ 0.84 (t, 6H, *J* = 7.2 Hz), 1.15–1.44 (m, 28H), 1.58 (quin, 4H, *J* = 7.2 Hz), 3.05–3.14 (m, 4H), 5.92 (brs, 2H), 7.05 (s, 2H), 7.16 (s, 2H), 7.39 (s, 2H), 7.69 (s, 4H); ^{13}C NMR (100 MHz, DMSO-*d*$_6$) δ 13.9, 22.0, 26.6, 28.5, 28.6, 28.8, 28.9, 29.0, 31.2, 42.8, 113.8, 114.6, 127.0, 132.1, 139.4, 140.5, 149.7, 167.8; HRMS (EI) calcd for $C_{40}H_{56}N_2O_4$ $[M^+]$: 628.4226, found 628.4256.

5,5”-Bis(ethylamino)-[1,1’:4’,1”-terphenyl]-3,3”-dicarboxylic acid (8b).

A solution of the compound **7b** (0.27 g, 0.5 mmol) in xylene/ethanol (2:1, 7.5 mL) and 16.5 M KOH (2.5 mL) was stirred at 150 °C for 48 h. The reaction mixture was cooled in an ice-water bath and neutralized with 2 M HCl with cooling and subsequently extracted with chloroform. The organic layer was washed with water, and concentrated in vacuo. The residue was purified by trituration using distilled water to give product **8b** as a white solid (58 mg, 0.14 mmol, 29%). M.p. >300 °C over. FT-IR (KBr): 3462, 2980, 1646 cm^{-1}. ^1H NMR (400 MHz, CD_3OD) δ 1.29 (t, 6H, *J* = 6.8 Hz), 3.22 (q, 4H, *J* = 6.8 Hz), 7.12 (s, 2H), 7.27 (s, 2H), 7.58 (s, 2H), 7.70 (s, 4H); ^{13}C NMR (100 MHz, CD_3OD) δ 14.7, 39.2, 113.4, 116.6, 117.6, 128.3, 133.2, 141.4, 142.9, 151.0, 170.6; HRMS (FAB) calcd for $C_{24}H_{25}N_2O_4$ $[M+H]^+$: 405.1808, found 405.1809.

Cylindrical macrocycles 1a.

To a solution of the compound **8a** (0.16 g, 0.25 mmol) in 1,1,2,2-tetrachloroethane (5 mL) under argon atmosphere was added dichlorotriphenylphosphorane (0.41 g, 1.2 mmol, 4.8 eq.) and stirred at 120 °C for 3 h. After cooling, the reaction mixture was poured into water, and extracted with chloroform. The organic layer was washed with 2 M HCl, brine, sat. $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography (*n*-hexane : ethyl acetate = 2:1), followed by preparative GPC (chloroform as an eluent) to obtain **1a** as a yellow solid of the diastereomeric mixture (24 mg, 13 μmol, 16%). Optical resolution was carried out by chiral high performance liquid chromatography with a Daicel CHIRALPAK IA column (1.0 cm (i.d.) × 25 cm) using dichloromethane as an eluent at a flow rate of 1.9 mL/min (elution time 5.7 min, 12.4 min, 21.5 min). HRMS (ESI) calcd for $C_{120}H_{157}N_6O_6$ $[M+H]^+$: 1778.2164, found 1778.2185.

(chiral)
M.p. 116–118 °C. FT-IR (KBr): 2924, 2853, 1653, 1591 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.54 (t, 18H, *J* = 7.2 Hz), 1.19–1.42 (m, 84H), 1.60–1.73 (m, 12H), 3.53–3.60 (m, 6H), 4.05–4.12 (m, 6H), 6.76 (s, 12H), 6.89 (t, 6H, *J* = 1.6 Hz), 7.08 (t, 6H, *J* = 1.6 Hz), 7.18 (t, 6H, *J* = 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.8, 27.0, 27.9, 29.4, 29.4, 29.6, 29.7, 32.0, 49.3, 125.4, 126.2, 127.8, 130.2, 138.7, 139.5, 140.8, 142.9, 169.7.

(meso)
M.p. 122–124 °C. FT-IR (KBr): 2926, 2852, 1651, 1591 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (t, 18H, *J* = 6.8 Hz), 1.19–1.42 (m, 84H), 1.55–1.72 (m, 12H), 3.51–3.58 (m, 6H), 4.03–4.10 (m, 6H), 6.76 (s, 12H), 6.89 (t, 6H, *J* = 1.6 Hz), 7.00 (t, 6H, *J* = 1.6 Hz), 7.25 (t, 6H, *J* = 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 22.8, 26.9, 27.8, 29.4, 29.4, 29.6, 29.6, 32.0, 49.4, 125.2, 126.2, 127.8, 130.3, 138.8, 139.5, 140.8, 142.8, 169.7.

Cylindrical macrocycles 1b.

To a solution of the compound **8b** (0.12 g, 0.30 mmol) in 1,1,2,2-tetrachloroethane (6 mL) under argon atmosphere was added dichlorotriphenylphosphorane (0.49 g, 1.4 mmol, 4.8 eq.) and stirred at 120 °C for 4.5 h. After cooling, the reaction mixture was poured into water, and extracted with chloroform. The organic layer was washed with 2 M HCl, brine, sat. $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography (chloroform : ethyl acetate : methanol = 25:20:1), followed by preparative GPC (chloroform as an eluent) to obtain **1b** as a yellow solid of the diastereomeric mixture (16 mg, 15 μmol, 14%). Optical resolution was carried out by chiral high performance liquid chromatography with a Daicel CHIRALPAK IA column (1.0 cm (i.d.) × 25 cm) using *n*-hexane : dichloromethane (1:3 in volume ratio) as an eluent at a flow rate of 1.9 mL/min (elution time 4.4 min, 28.2 min, 34.0 min). HRMS (ESI) calcd for $C_{72}H_{61}N_6O_6$ $[M+H]^+$: 1105.4647, found 1105.4670.

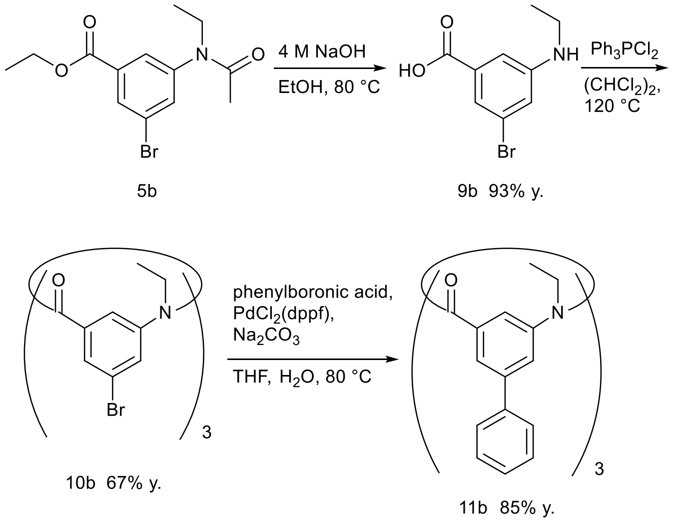
(chiral)

M.p. >300 °C. FT-IR (KBr): 1646, 1590 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.28 (t, 18H, J = 7.2 Hz), 3.71 (sext, 6H, J = 7.2 Hz), 4.13 (sext, 6H, J = 6.8 Hz), 6.77 (s, 12H), 6.91 (t, 6H, J = 1.2 Hz), 7.11 (t, 6H, J = 1.2 Hz), 7.21 (t, 6H, J = 1.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 13.2, 44.0, 125.5, 126.2, 127.8, 130.3, 138.7, 139.5, 140.9, 142.5, 169.6.

(meso)

M.p. >300 °C. FT-IR (KBr): 1651, 1591 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.25 (t, 18H, J = 7.2 Hz), 3.69 (sext, 6H, J = 6.8 Hz), 4.13 (sext, 6H, J = 7.2 Hz), 6.77 (s, 12H), 6.91 (t, 6H, J = 1.6 Hz), 7.02 (t, 6H, J = 1.6 Hz), 7.28 (t, 6H, J = 1.2 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 13.1 , 44.1, 125.3, 126.3, 127.8, 130.4, 138.7, 139.4, 140.9, 142.4, 169.6.

Calix[3]aramide 11b



3-Bromo-5-(ethylamino)benzoic acid (9b).

A solution of the compound **5b** (1.7 g, 5.5 mmol) in ethanol (28 mL) and 4 M NaOH (28 mL) was stirred at 80 °C for overnight. The reaction mixture was cooled in an ice-water bath and neutralized with 2 M HCl with cooling and subsequently extracted with ethyl acetate. The organic layer was washed with water and brine, dried over Na$_2$SO$_4$, and concentrated in vacuo. The residue was purified by toluene azeotrope and trituration using *n*-hexane to give product **9b** as a brown solid (1.2 g, 5.2 mmol, 93 %). M.p. 133–136 °C. FT-IR (KBr): 3405, 2965, 1687, 1597 cm^{-1}. ^{1}H NMR (400 MHz, CDCl$_3$) δ 1.27 (t, 3H, J = 7.2 Hz), 3.18 (q, 2H, J = 7.2 Hz), 6.46 (brs, 2H), 6.92 (dd, 1H, J = 1.6, 2.0 Hz), 7.22 (dd, 1H, J = 1.2, 2.0 Hz), 7.52 (t, 1H, J = 1.6 Hz); ^{13}C NMR (100 MHz, CDCl$_3$) δ 14.6, 38.4, 113.0, 119.9, 121.4, 123.3, 131.6, 149.5, 171.2; HRMS (FAB) calcd for $C_9H_{11}{}^{79}BrNO_2$ [M+H]$^+$: 243.9970, found 243.9971.

Calix[3]aramide 10b.

To a solution of the compound **9b** (0.74 g, 3.0 mmol) in 1,1,2,2-tetrachloroethane (30 mL) under argon atmosphere was added dichlorotriphenylphosphorane (2.4 g, 7.4 mmol, 2.4 eq.) and stirred at 120 °C for 2 h. After cooling, the reaction mixture was poured into water, and extracted with chloroform. The organic layer was washed with 2 M HCl, brine, sat. $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography (chloroform : acetonitrile = 3:1), followed by preparative GPC (chloroform as an eluent) to obtain **10b** as a white solid (0.46 g, 0.68 mmol, 67 %). M.p. 261–263 °C. FT-IR (KBr): 3068, 2975, 2934, 2873, 1651, 1593, 1566 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.17 (t, 9H, J = 6.8 Hz), 3.76 (brs, minor 6H), 3.84 (q, major 6H, J = 6.8 Hz), 6.30 (brs, minor 3H), 6.81 (s, major 3H), 7.12 (s, major 3H), 7.23 (s, major 3H), 7.4–7.5 (m, minor 3H), 7.6–7.7 (m, minor 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.8, 45.1, 46.1, 123.1, 125.9, 130.0, 133.2, 140.1, 143.0, 168.2; HRMS (FAB) calcd for $C_{27}H_{25}{}^{79}Br_3N_3O_3$ $[M+H]^+$: 675.9439, found 675.9445.

Calix[3]aramide 11b.

A mixture of the compound **10b** (61 mg, 89 μmol), phenylboronic acid (41 mg, 0.34 mmol, 4.5 eq.), sodium carbonate (0.12 g, 1.1 mmol, 15 eq.) and $PdCl_2(dppf)$ (28 mg, 34 μmol, 0.45 eq.) in THF (2.5 mL) and water (2.5 mL) was stirred at 100 °C for 1.5 h under argon atmosphere. After cooling, the reaction mixture was poured into water, and extracted with ethyl acetate. The organic layer was washed with sat. $NaHCO_3$ and brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by silica gel column chromatography (chloroform : methanol = 249:1), followed by preparative GPC (chloroform as an eluent) to obtain **11b** as a pale orange solid (51 mg, 75 μmol, 85%). M.p. 230–232 °C. FT-IR (KBr): 2362, 1654, 1592 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (t, 9H, J = 7.2 Hz), 3.74 (sext, 3H, J = 6.4 Hz), 4.02 (sext, 3H, J = 6.4 Hz),6.47 (s, minor 3H), 6.90 (d, major 6H, J = 6.8 Hz), 6.91 (s, mjor 3H), 7.02 (s, major 3H), 7.10 (t, major 6H, J = 7.6 Hz), 7.21 (s, major 3H), 7.26 (t, major 3H, J = 8.0 Hz), 7.39 (s, minor 5H), 7.52 (s, minor 3H), 7.78 (s, minor 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.1, 44.5, 125.3, 126.2, 127.1, 128.0, 128.9, 129.7, 139.1, 139.4, 142.5, 142.8, 170.1; HRMS (FAB) calcd for $C_{45}H_{40}N_3O_3$ $[M+H]^+$: 670.3060, found 670.3061.

3. Characterization of compounds

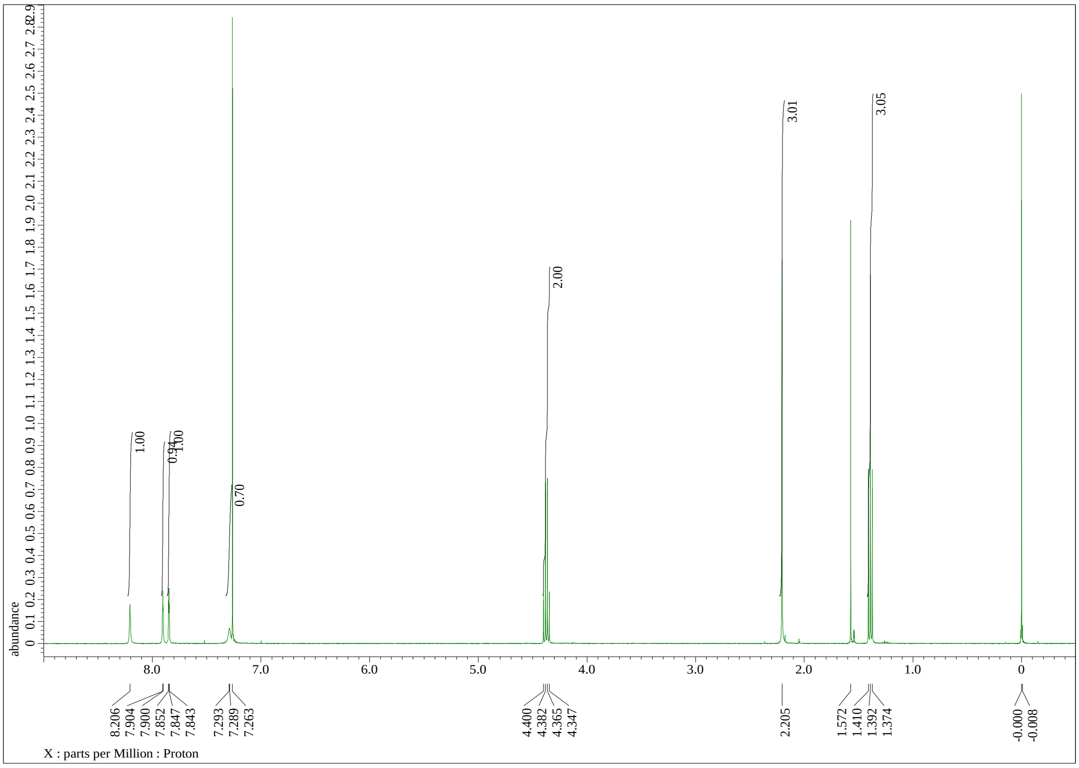


Fig. S1 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **ethyl 3-acetamido-5-bromobenzoate (4)**.

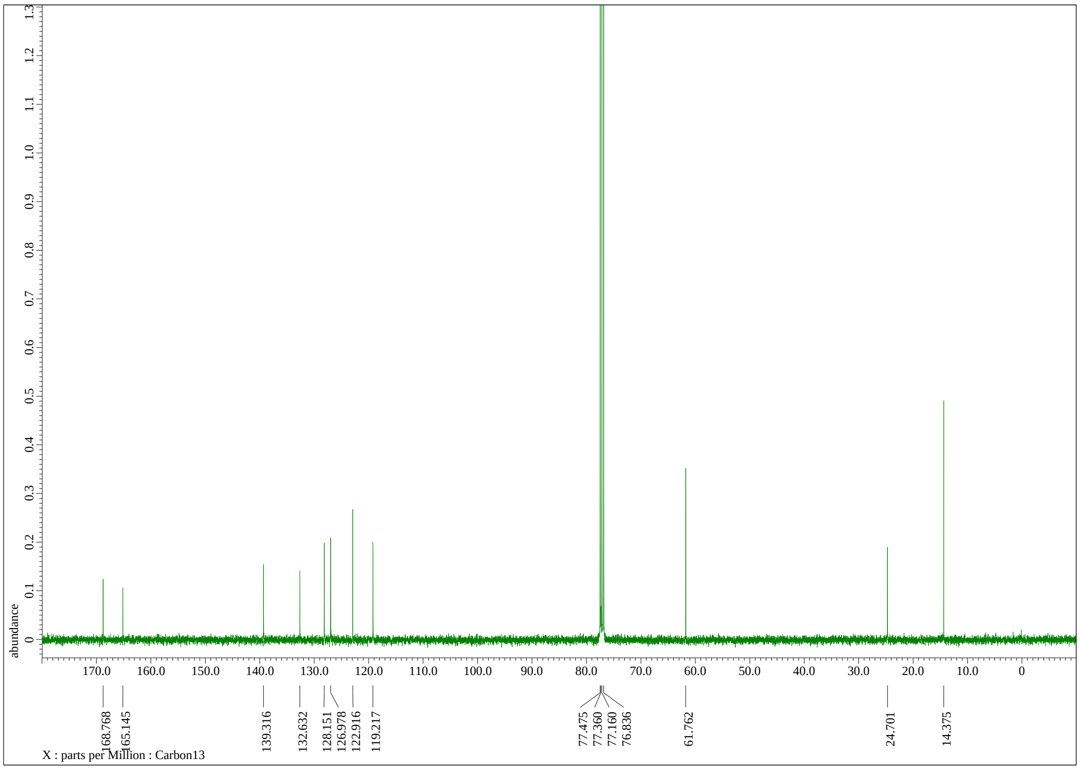


Fig. S2 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **ethyl 3-acetamido-5-bromobenzoate (4)**.

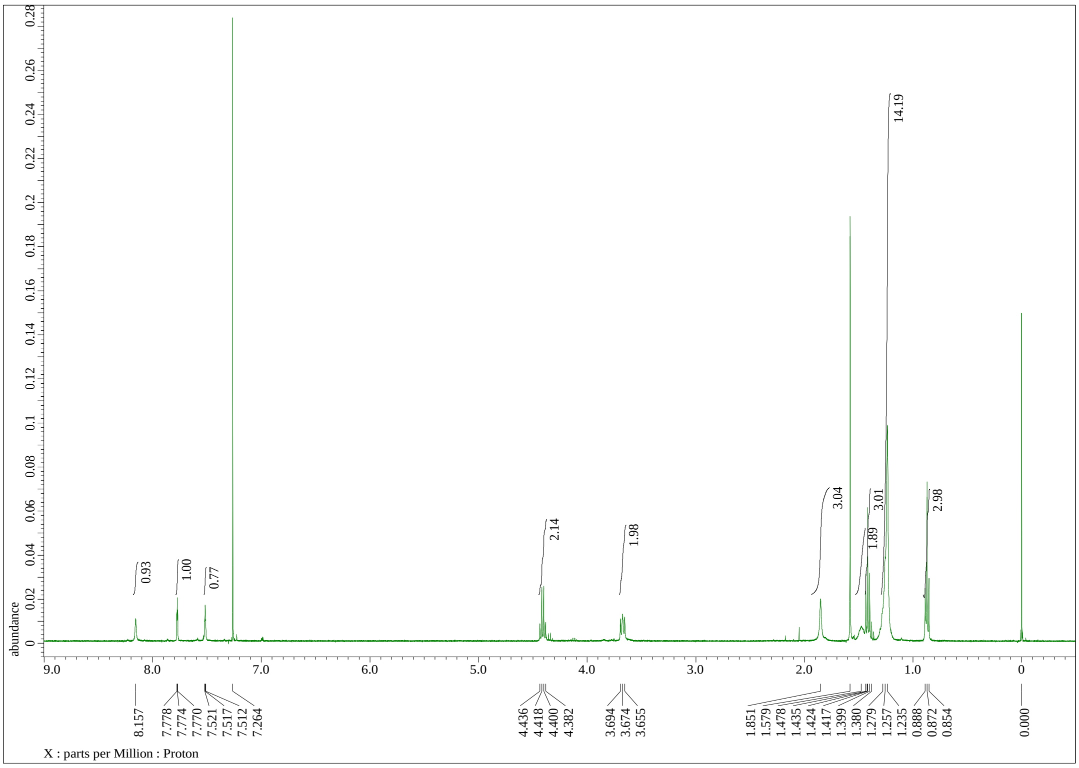


Fig. S3 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **ethyl 3-bromo-5-(*N*-decylacetamido)benzoate (5a)**.

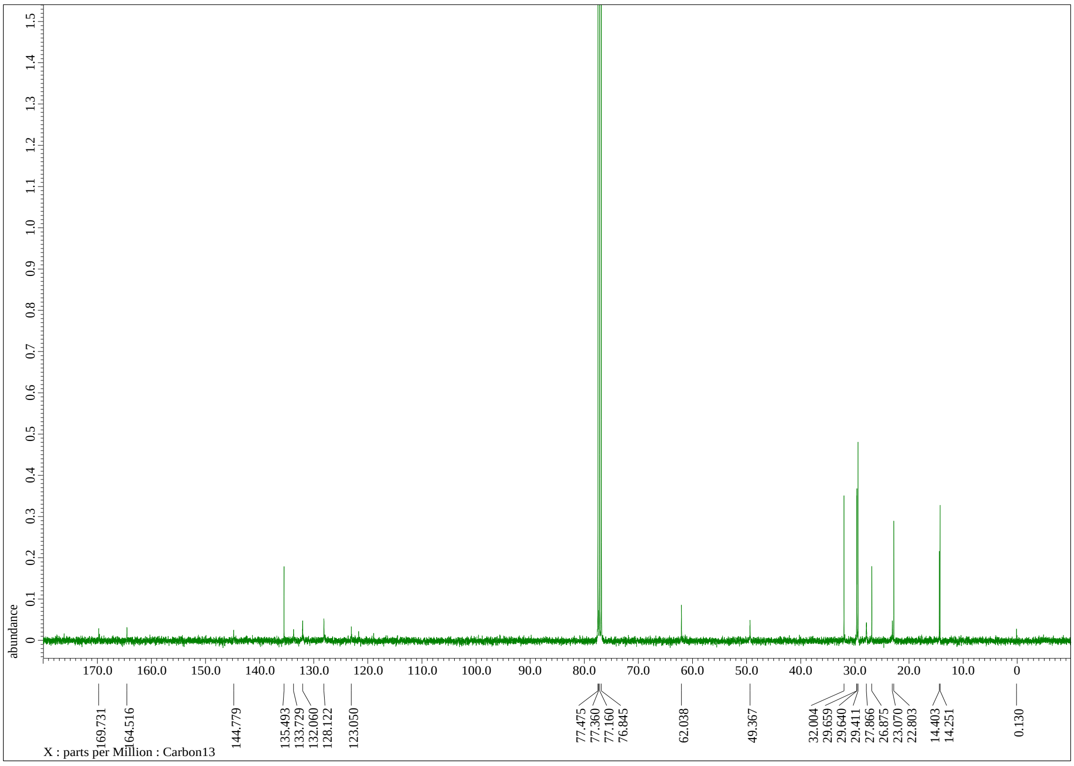


Fig. S4 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **ethyl 3-bromo-5-(*N*-decylacetamido)benzoate (5a)**.

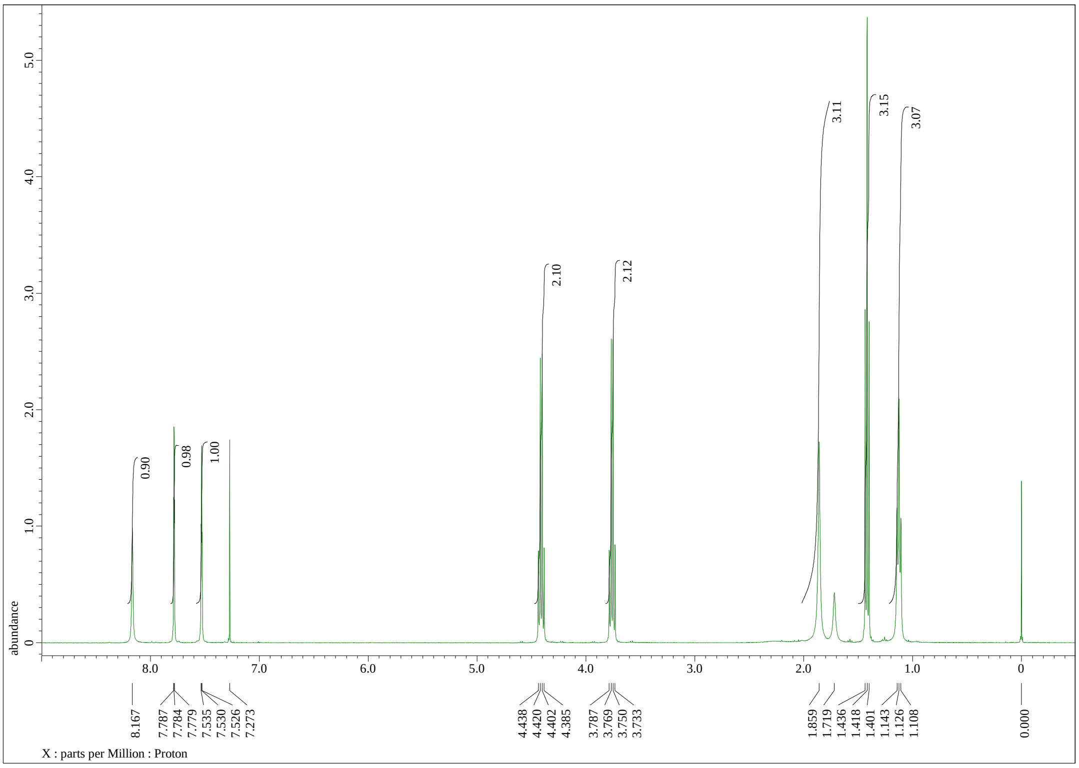


Fig. S5 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **ethyl 3-bromo-5-(*N*-ethylacetamido)benzoate (5b)**.

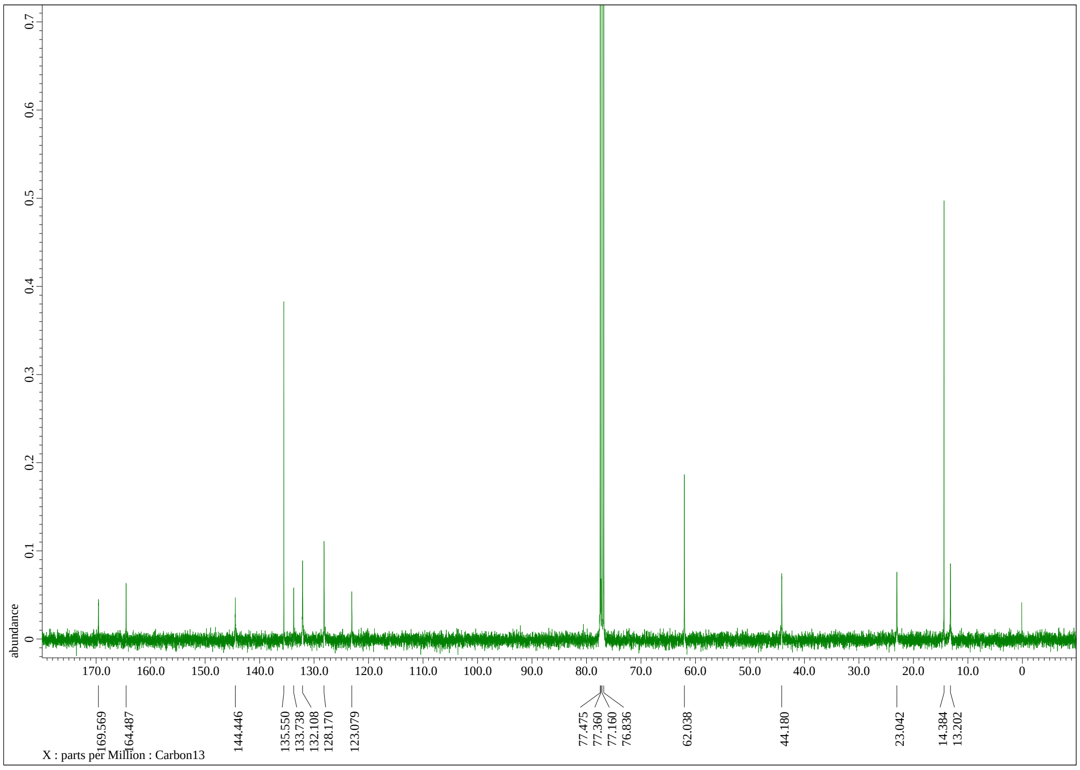


Fig. S6 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **ethyl 3-bromo-5-(*N*-ethylacetamido)benzoate (5b)**.

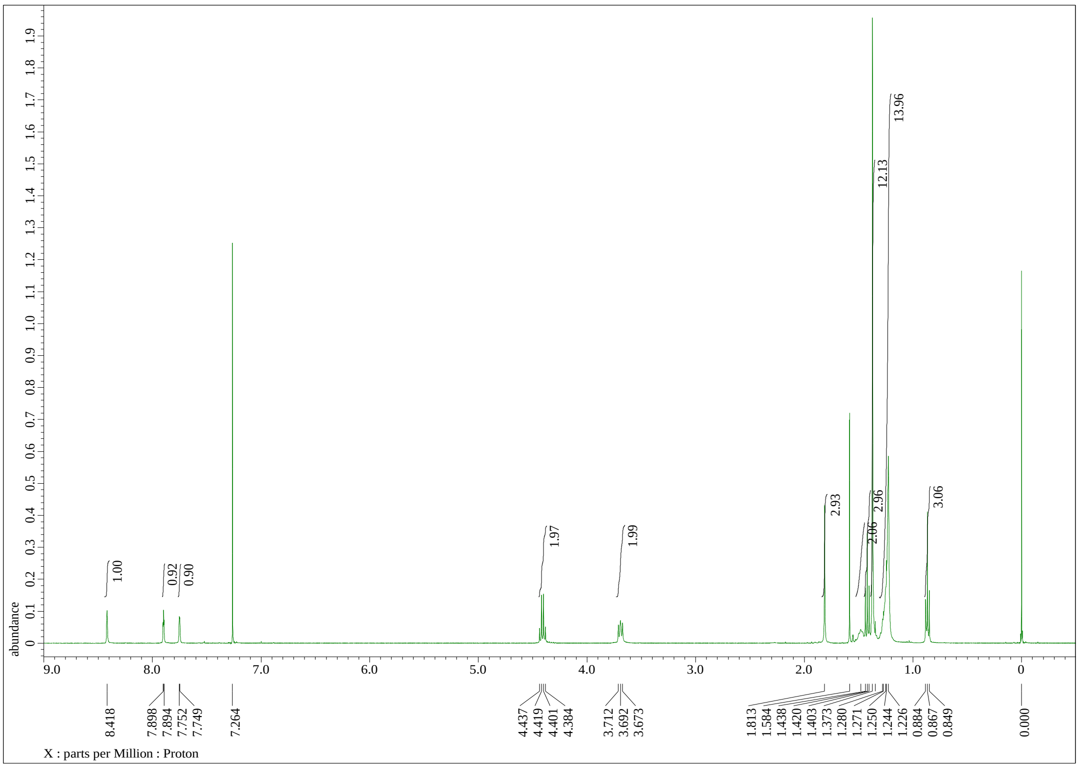


Fig. S7 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of

ethyl 3-(*N*-decylacetamido)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (6a).

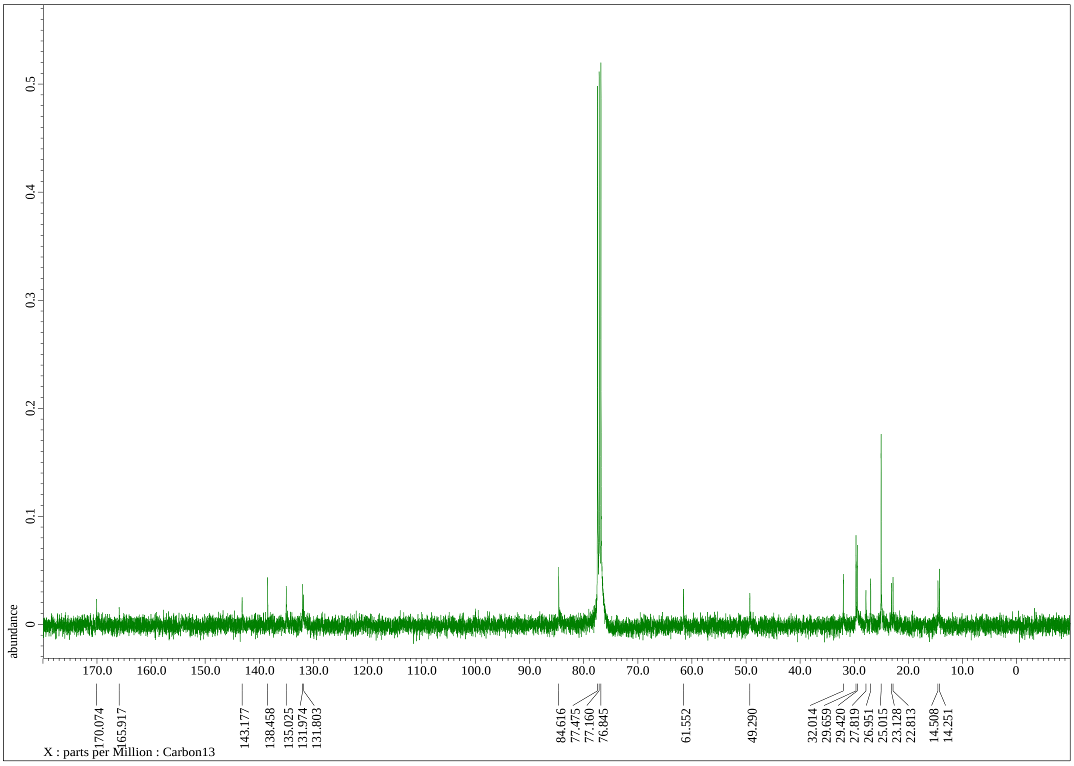


Fig. S8 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of

ethyl 3-(*N*-decylacetamido)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (6a).

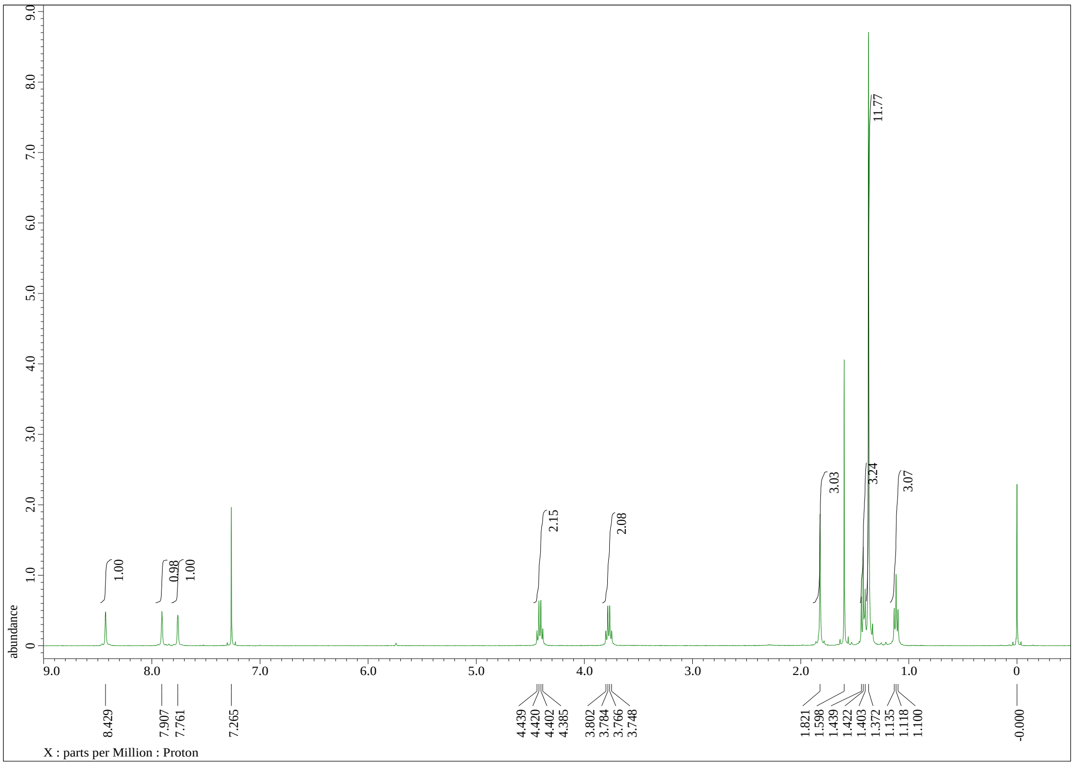


Fig. S9 ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of

ethyl 3-(*N*-ethylacetamido)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (6b).

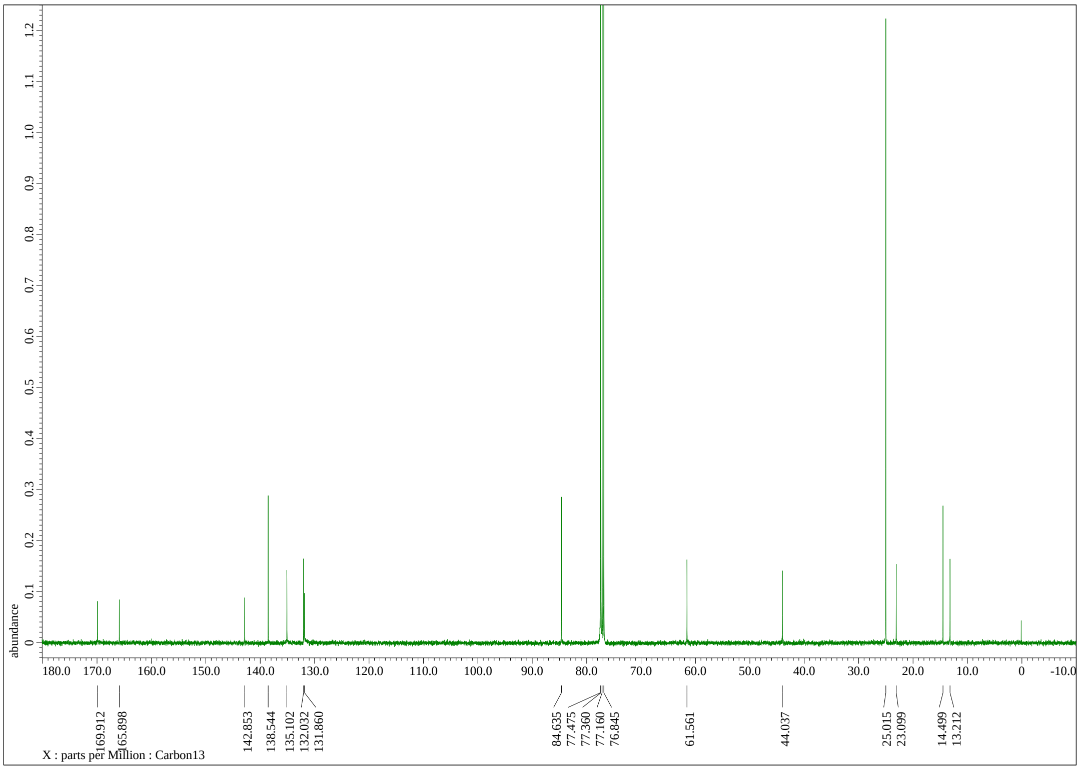


Fig S10 ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of

ethyl 3-(*N*-ethylacetamido)-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (6b).

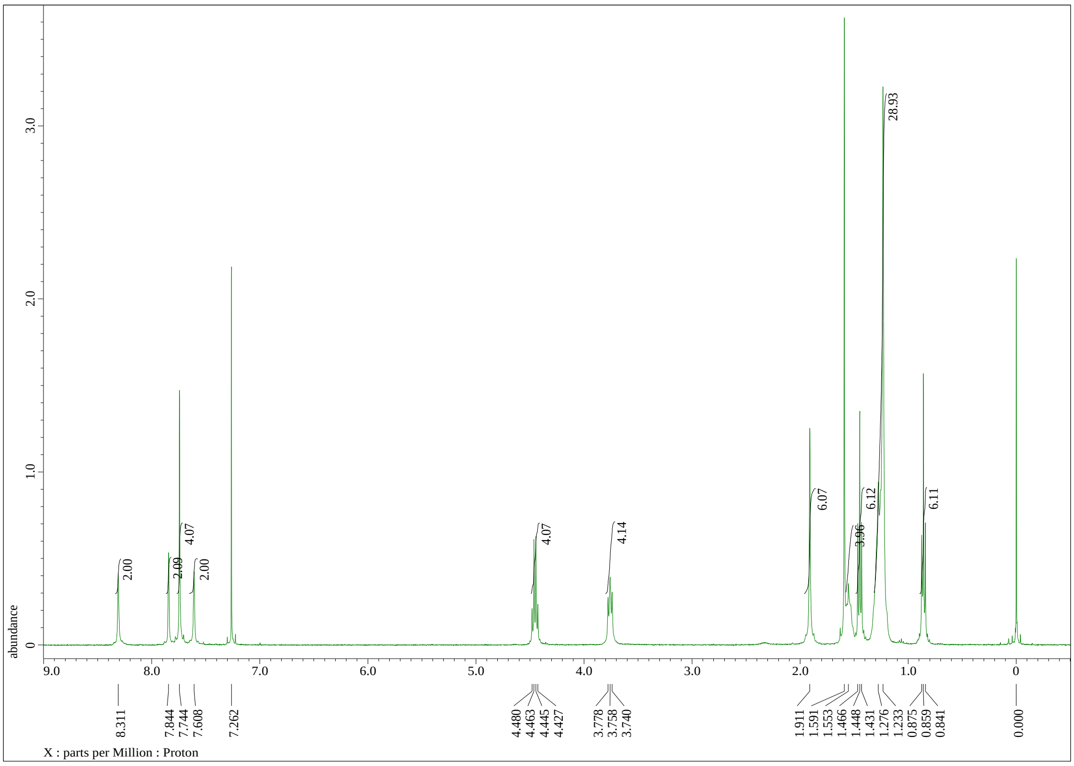


Fig. S11 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of

diethyl 5,5”-bis(*N*-decylacetamido)-[1,1’:4’,1”-terphenyl]-3,3”-dicarboxylate (7a).

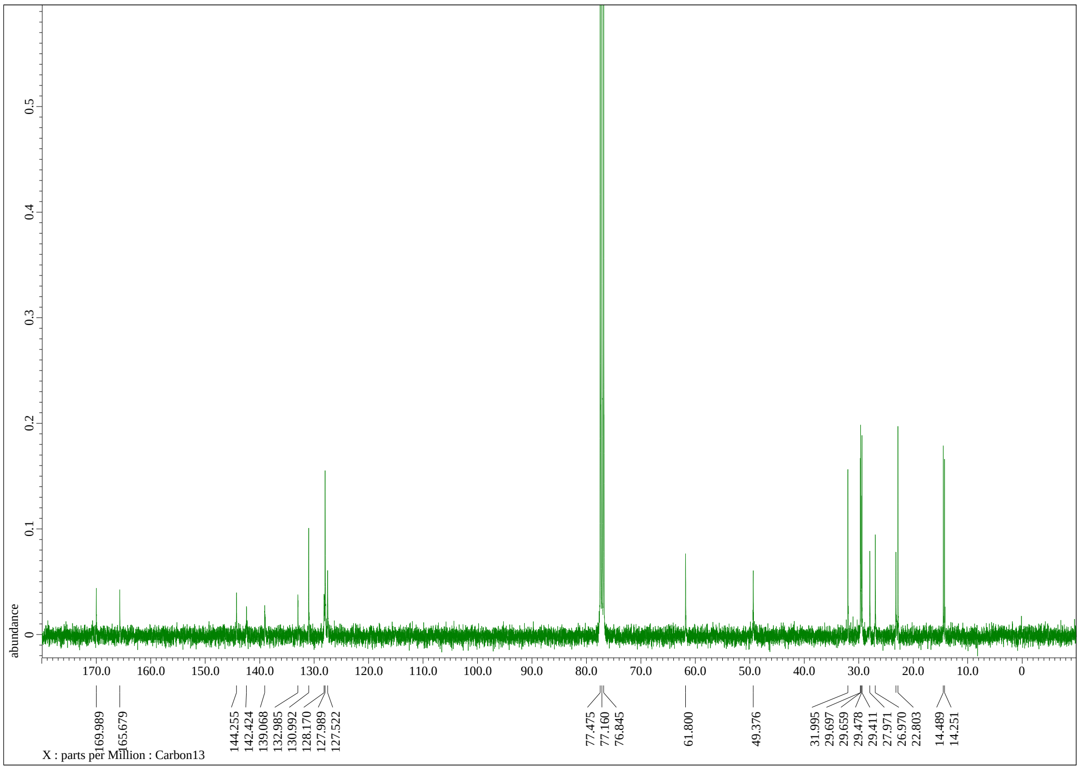


Fig. S12 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of

diethyl 5,5”-bis(*N*-decylacetamido)-[1,1’:4’,1”-terphenyl]-3,3”-dicarboxylate (7a).

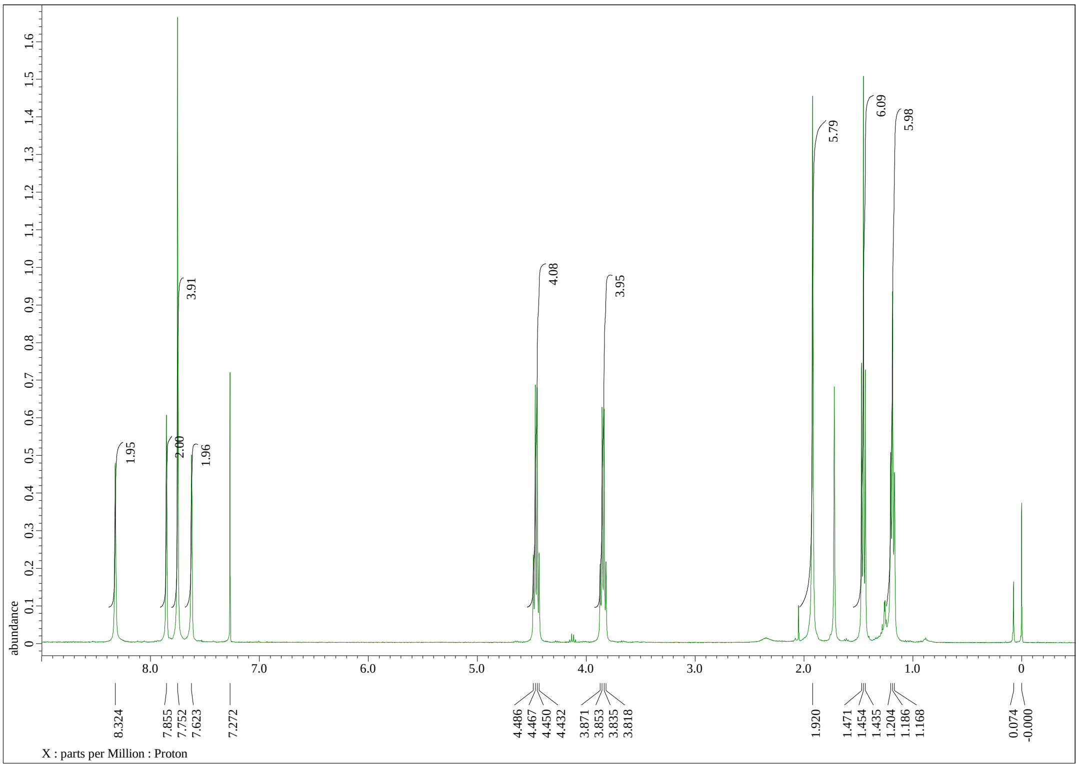


Fig. S13 ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of

diethyl 5,5”-bis(*N*-ethylacetamido)-[1,1’:4’,1”-terphenyl]-3,3”-dicarboxylate (7b).

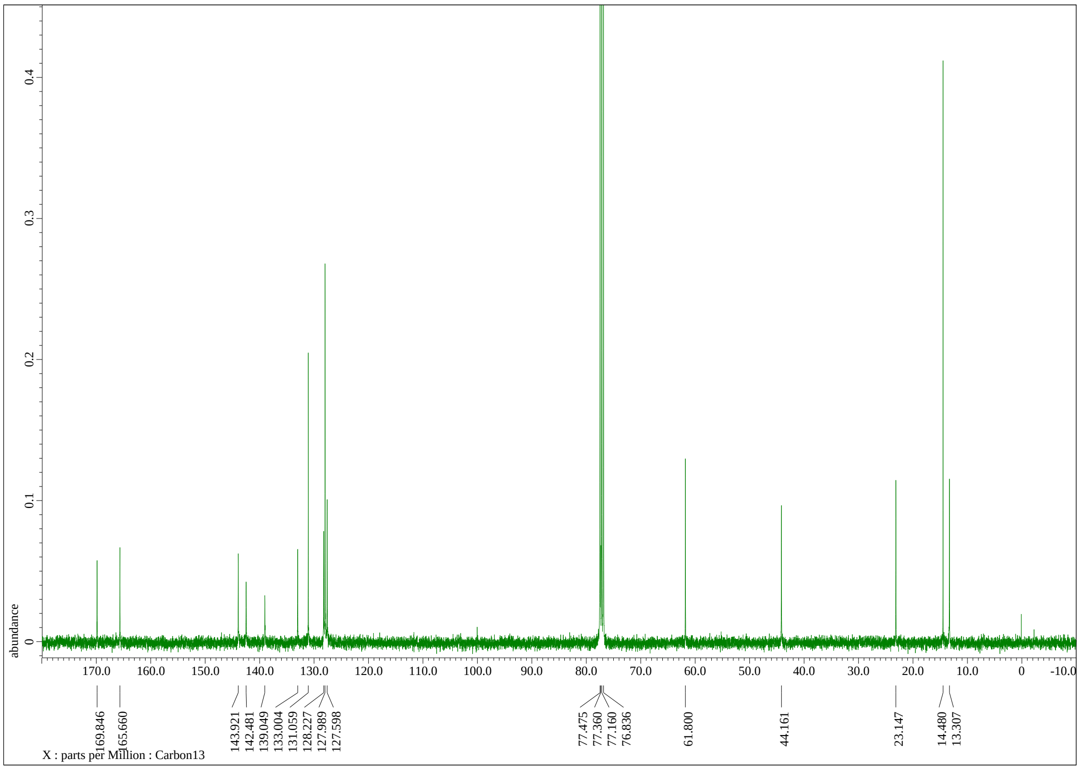
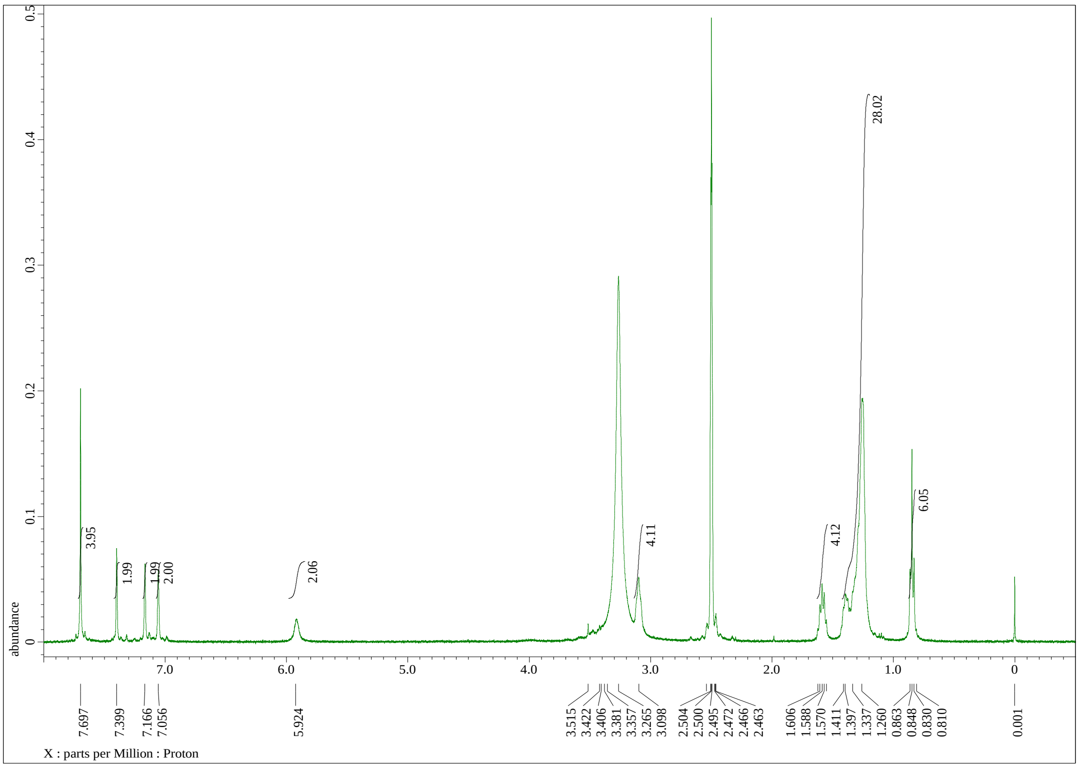


Fig. S14 ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of

diethyl 5,5”-bis(*N*-ethylacetamido)-[1,1’:4’,1”-terphenyl]-3,3”-dicarboxylate (7b).



Fig, S15 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of

5,5”-bis(decylamino)-[1,1’:4’,1”-terphenyl]-3,3”-dicarboxylic acid (8a).

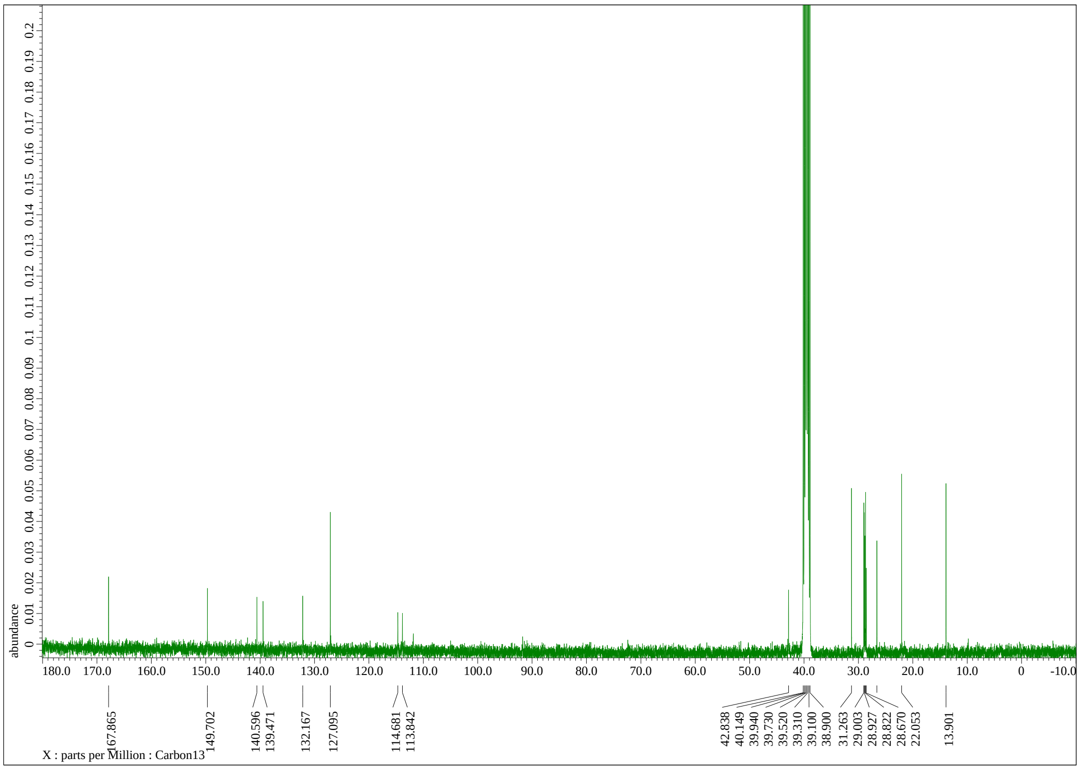


Fig. S16 ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of

5,5”-bis(decylamino)-[1,1’:4’,1”-terphenyl]-3,3”-dicarboxylic acid (8a).

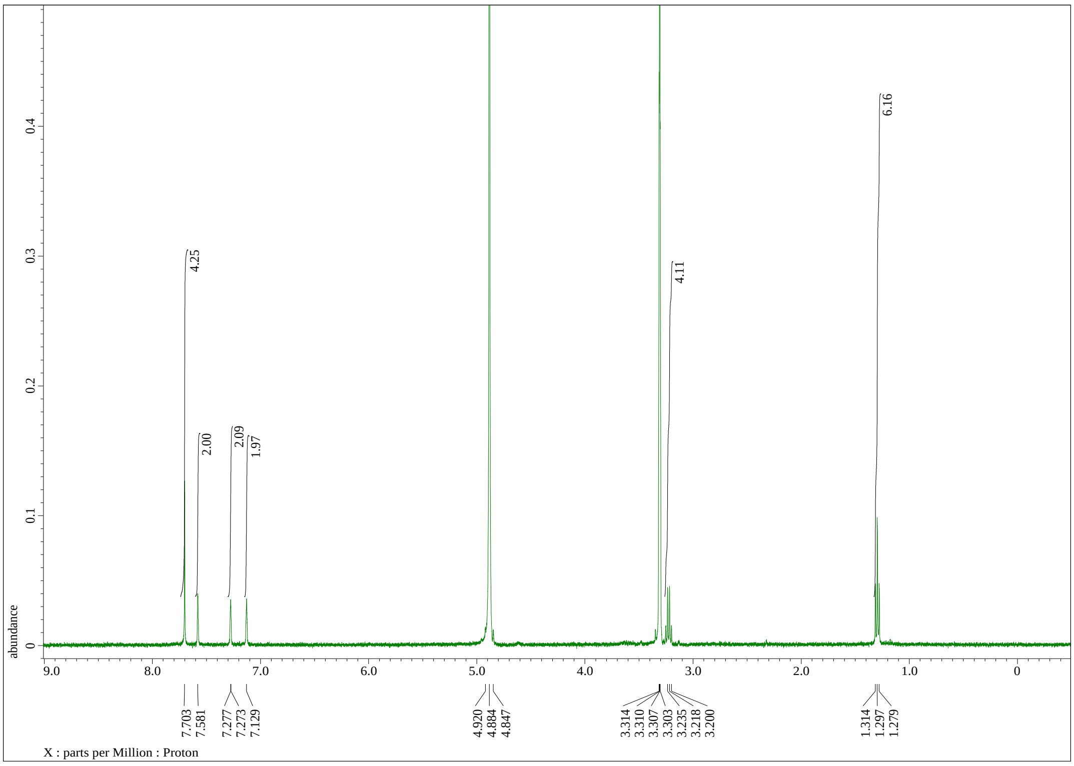


Fig. S17 ^{1}H NMR (400 MHz, CD_3OD) spectrum of

5,5”-bis(ethylamino)-[1,1’:4’,1”-terphenyl]-3,3”-dicarboxylic acid (8b).

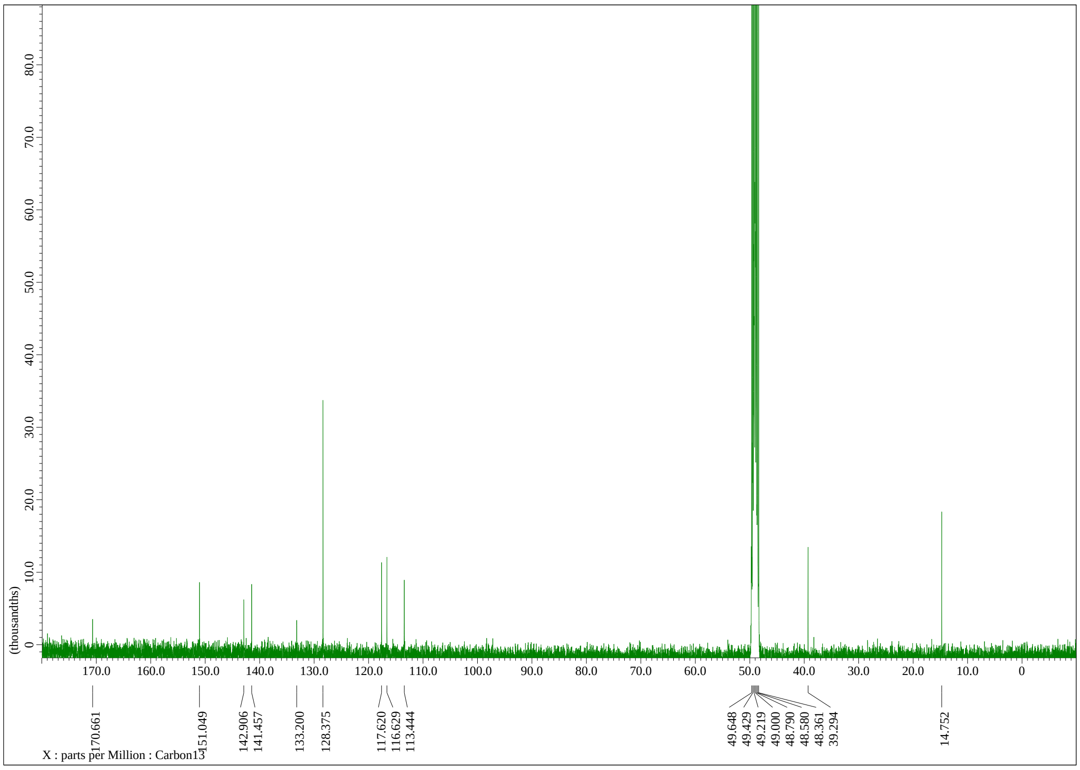


Fig. S18 ^{13}C NMR (100 MHz, CD_3OD) spectrum of

5,5”-bis(ethylamino)-[1,1’:4’,1”-terphenyl]-3,3”-dicarboxylic acid (8b).

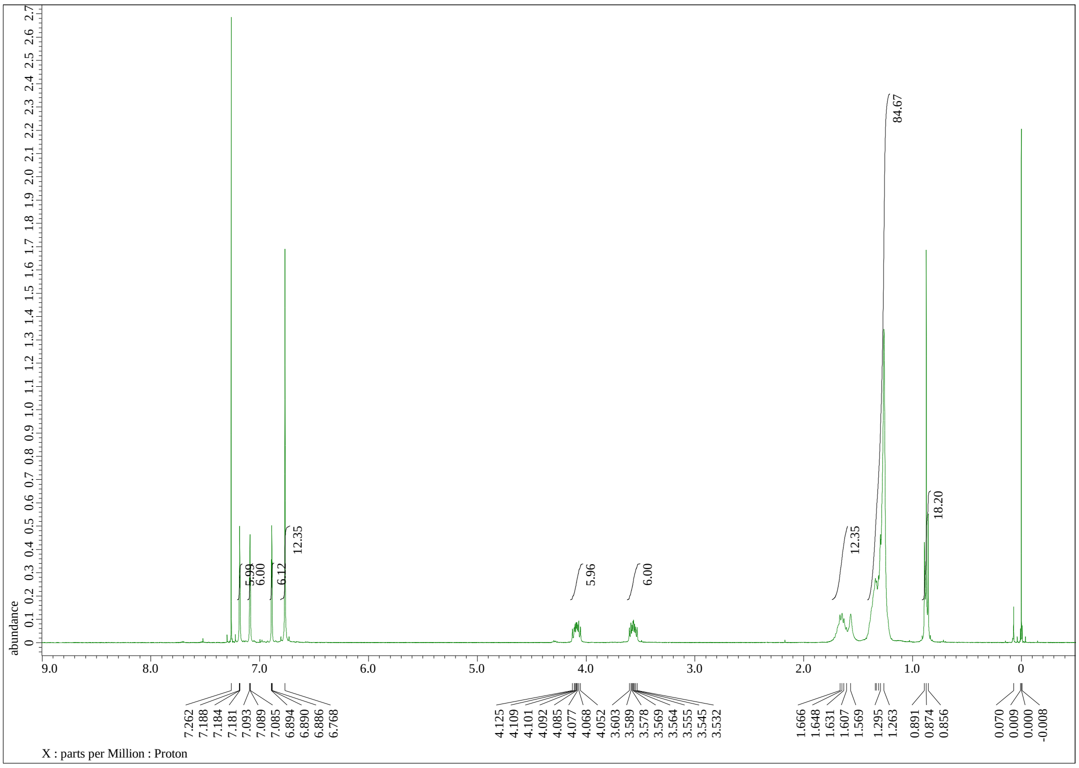


Fig. S19 ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **cylindrical macrocycle 1a**–(*PP*).

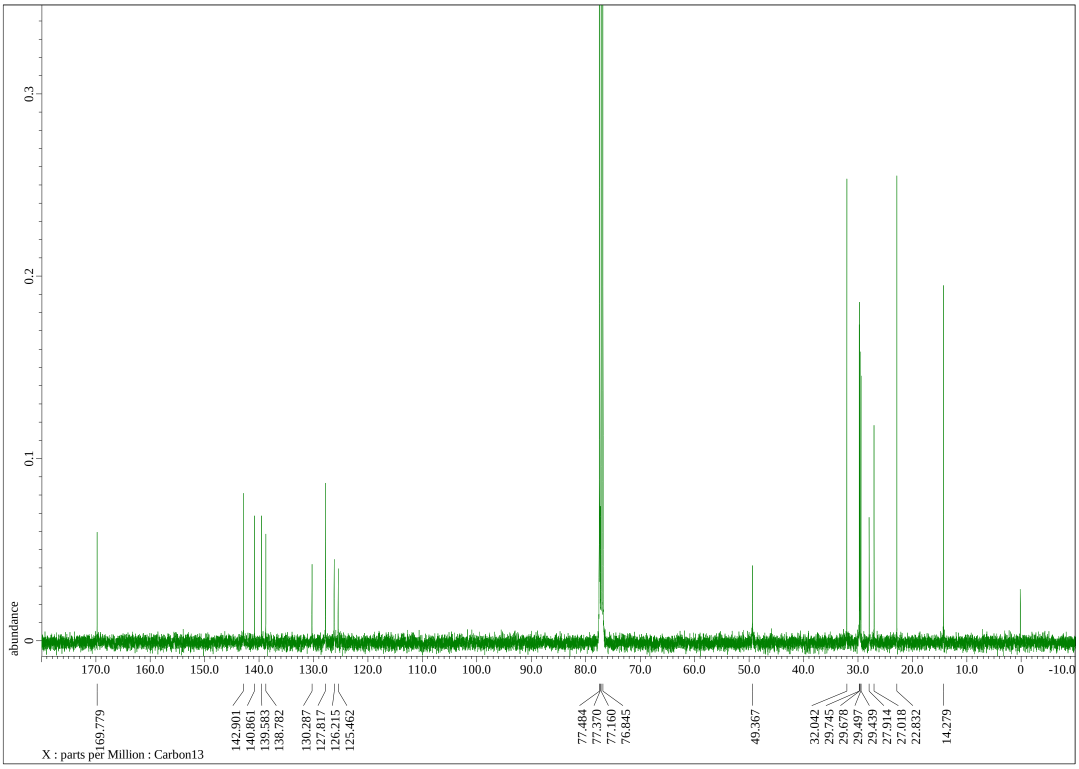


Fig. S20 ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of **cylindrical macrocycle 1a**–(*PP*).

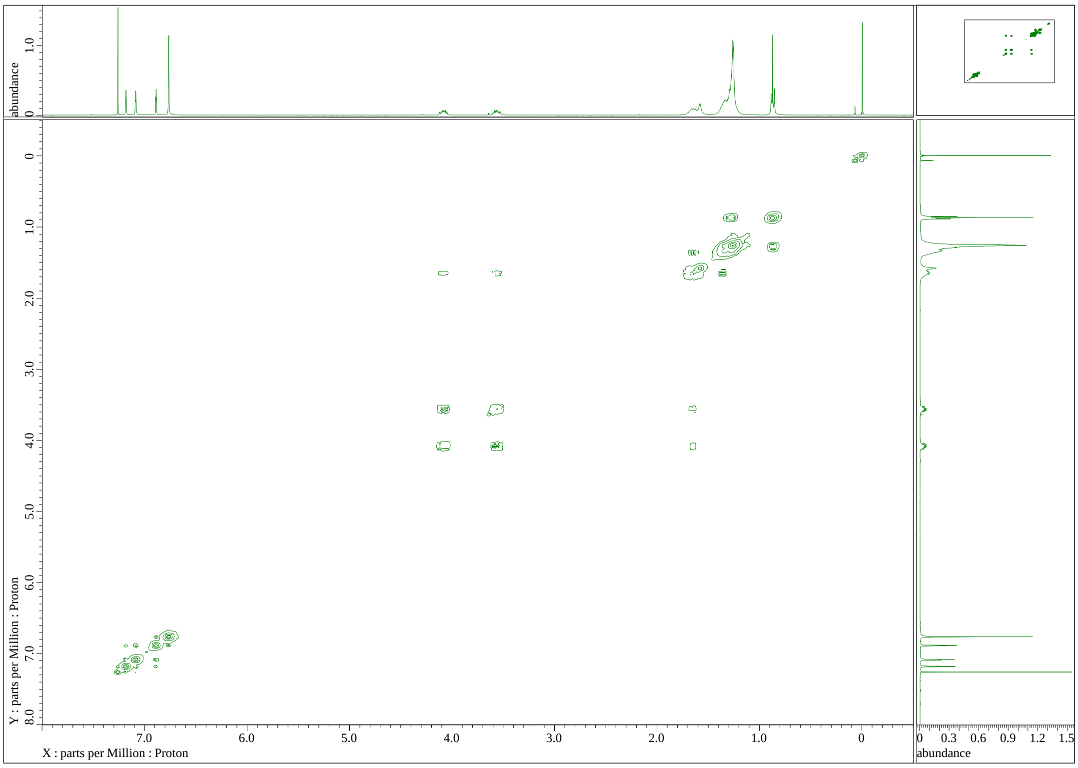


Fig. S21 ^{1}H–^{1}H COSY (CDCl$_3$) spectrum of **cylindrical macrocycle 1a**–(*PP*).

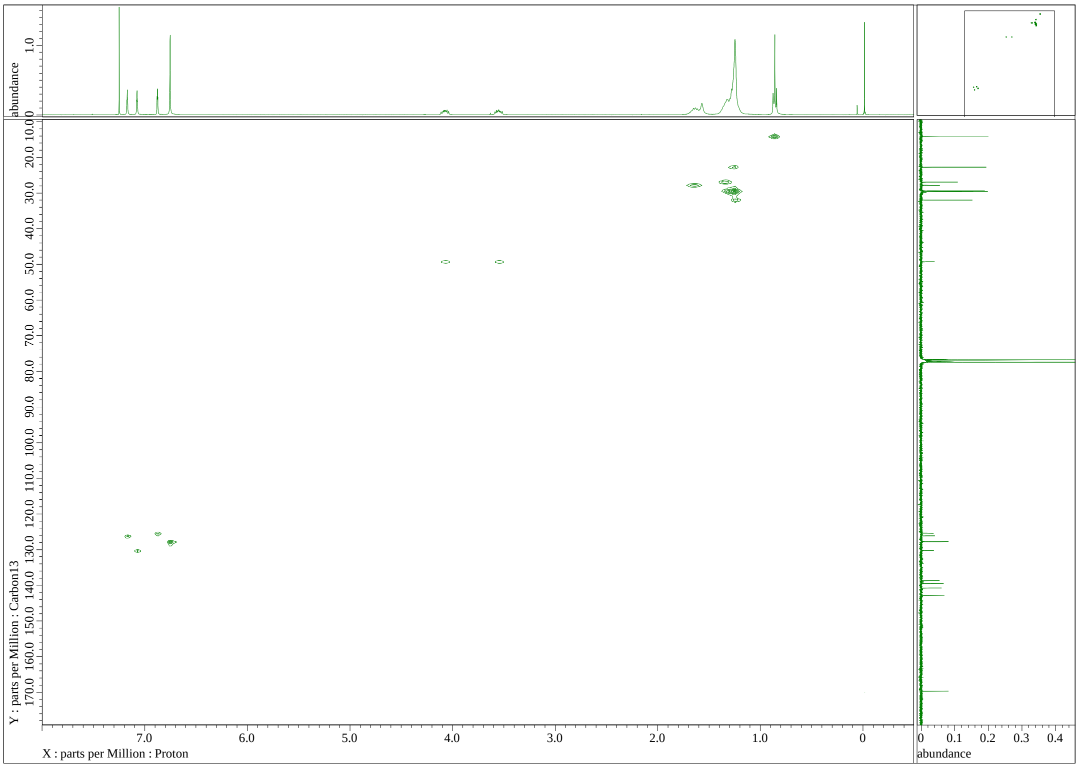


Fig. S22 ^{1}H–^{13}C HSQC (CDCl$_3$) spectrum of **cylindrical macrocycle 1a**–(*PP*).

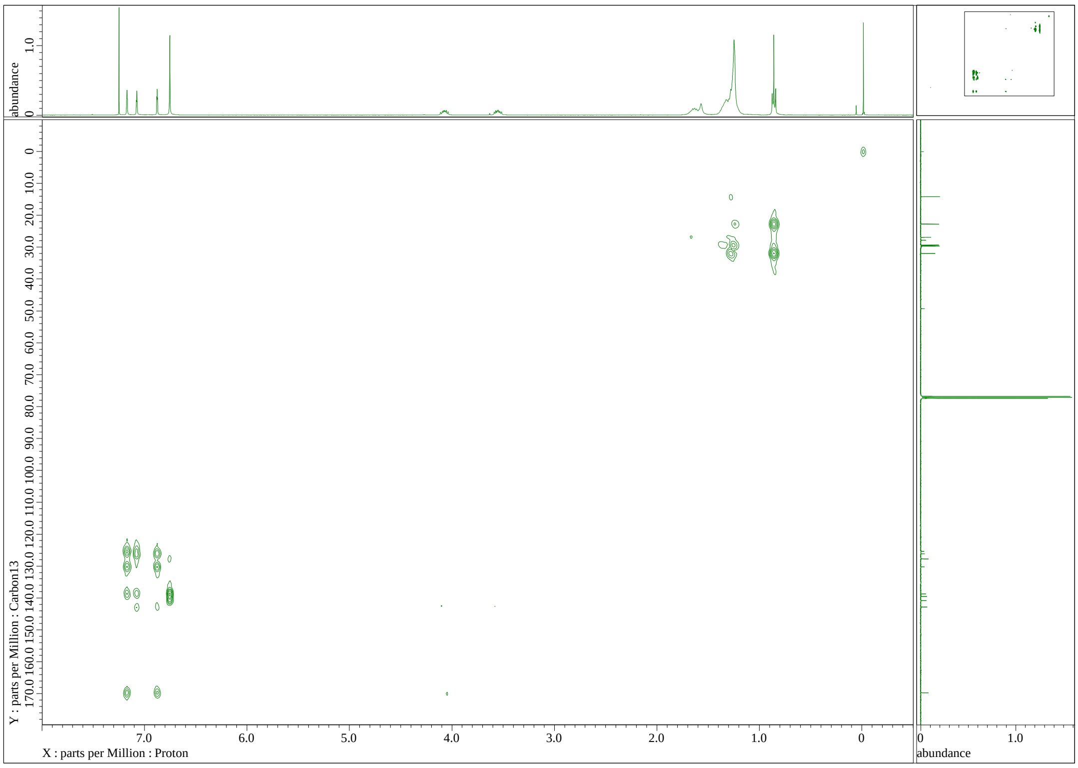


Fig. S23 ^{1}H–^{13}C HMBC (CDCl$_3$) spectrum of **cylindrical macrocycle 1a–(*PP*).**

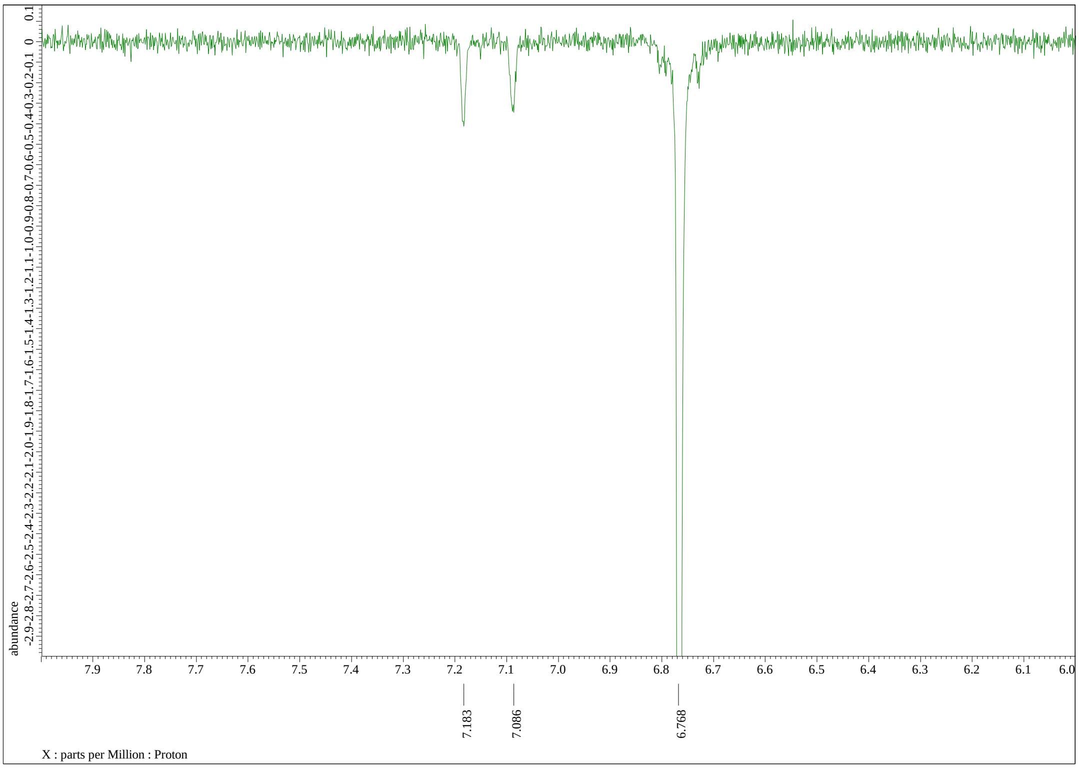


Fig. S24 1D-NOE (CDCl$_3$) spectrum of **cylindrical macrocycle 1a–(*PP*).**

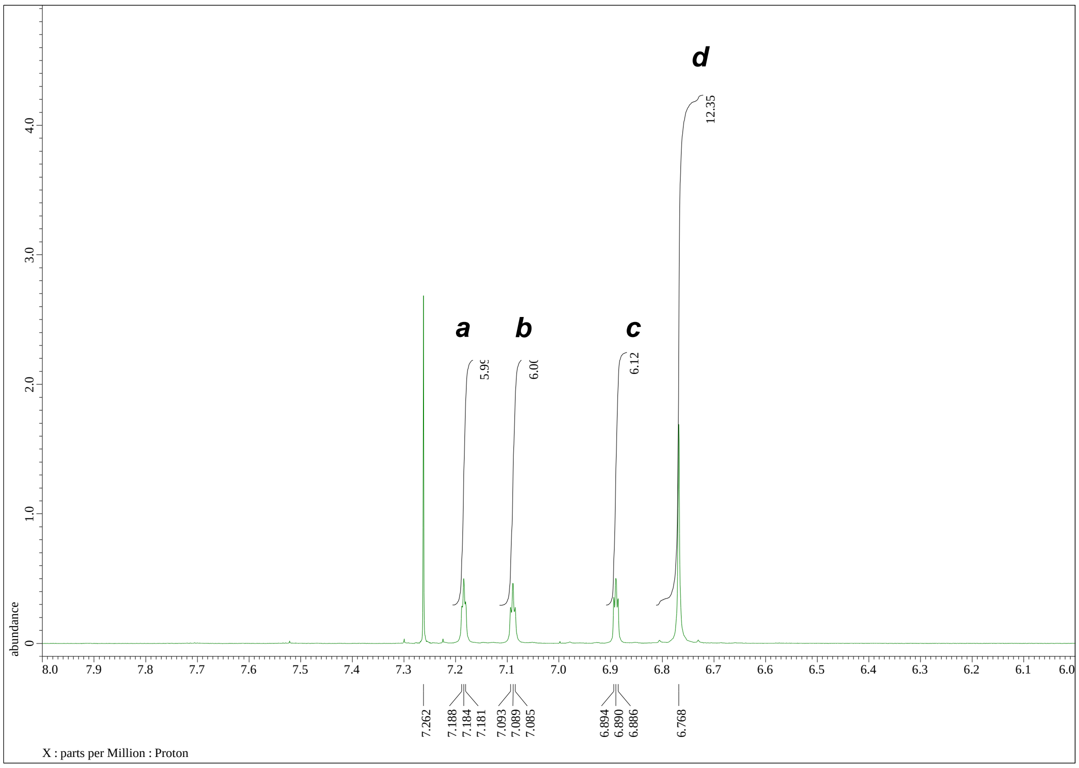
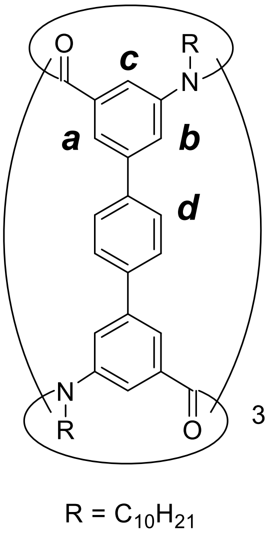


Fig. S25 The magnified chart of the aromatic region of ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **cylindrical macrocycle 1a–(*PP*).**



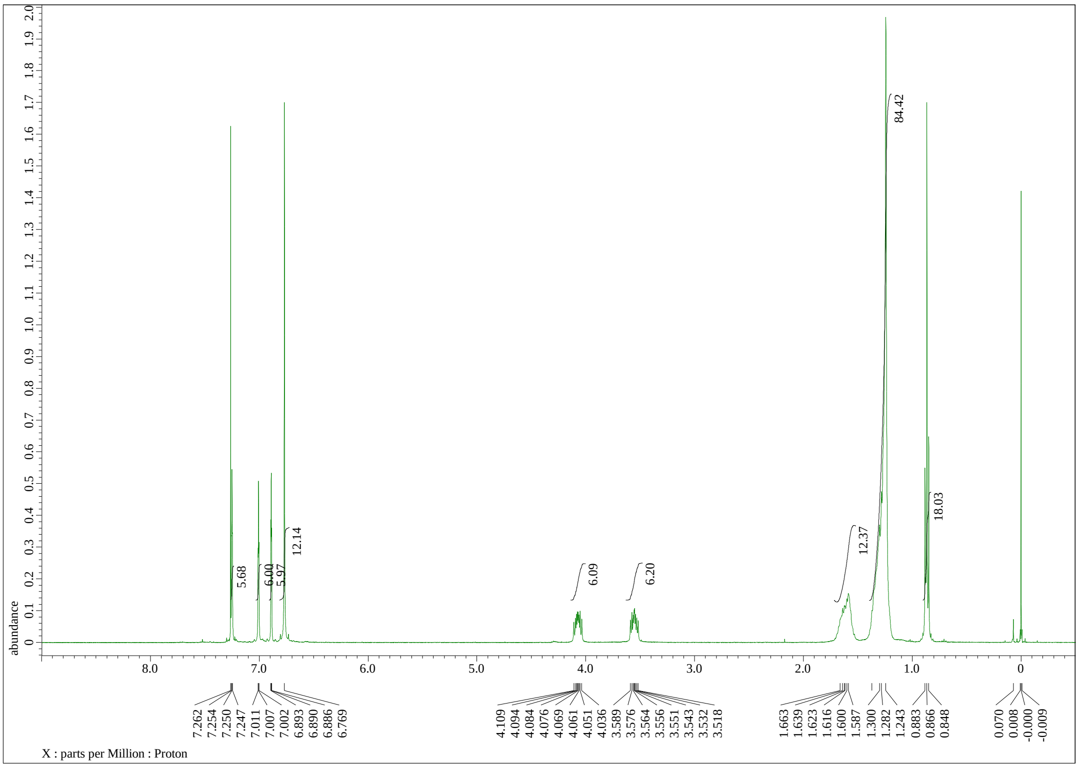


Fig. S26 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **cylindrical macrocycle 1a–(*PM*).**

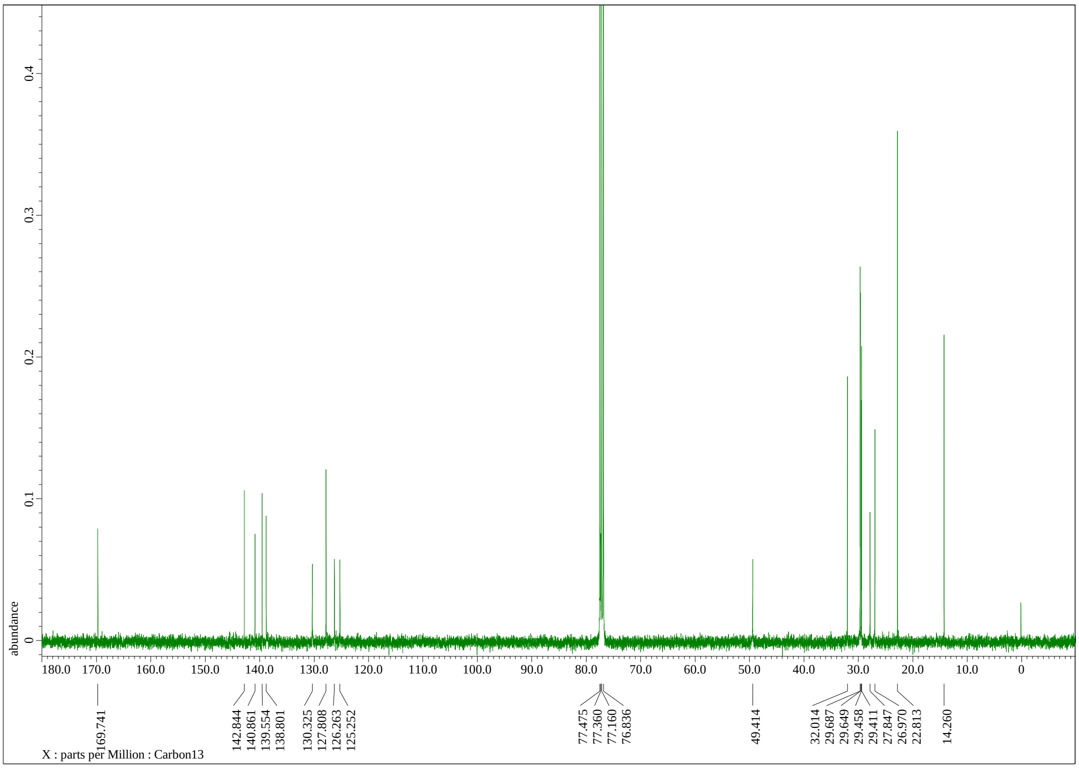


Fig. S27 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **cylindrical macrocycle 1a**–(*PM*).

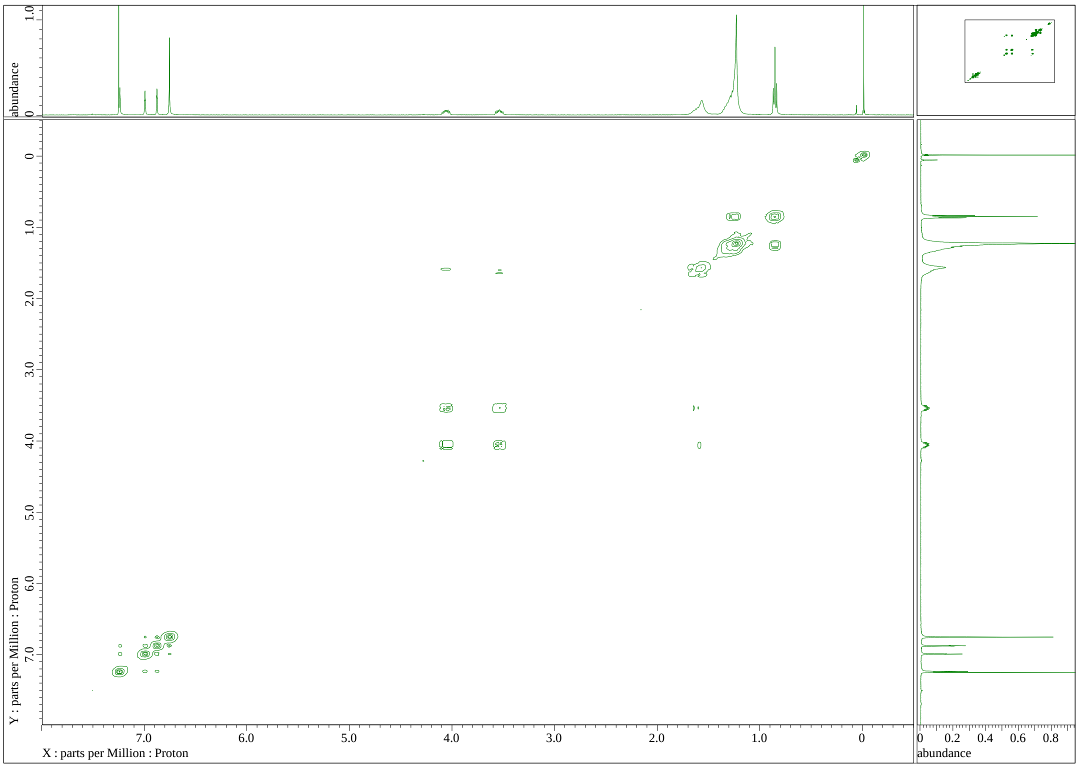


Fig. S28 ^{1}H–^{1}H COSY (CDCl$_3$) spectrum of **cylindrical macrocycle 1a**–(*PM*).

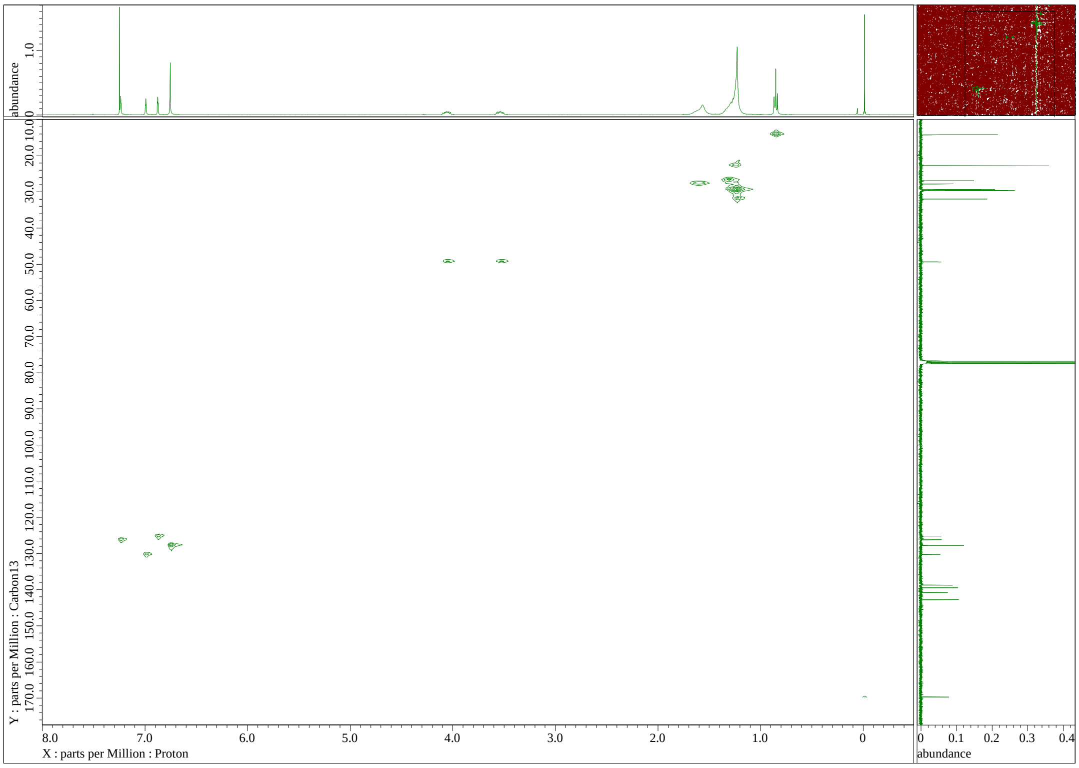


Fig. S29 ^{1}H–^{13}C HSQC (CDCl$_3$) spectrum of **cylindrical macrocycle 1a**–(*PM*).

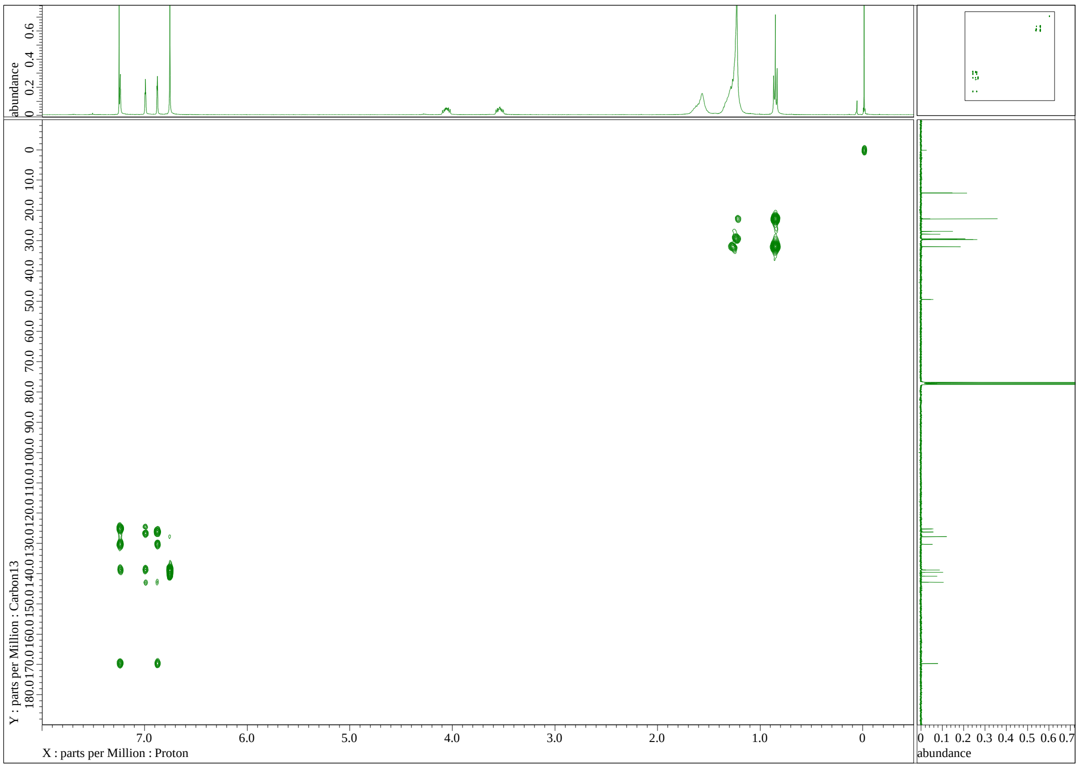


Fig. S30 ^{1}H–^{13}C HMBC ($CDCl_3$) spectrum of **cylindrical macrocycle 1a**–(*PM*).

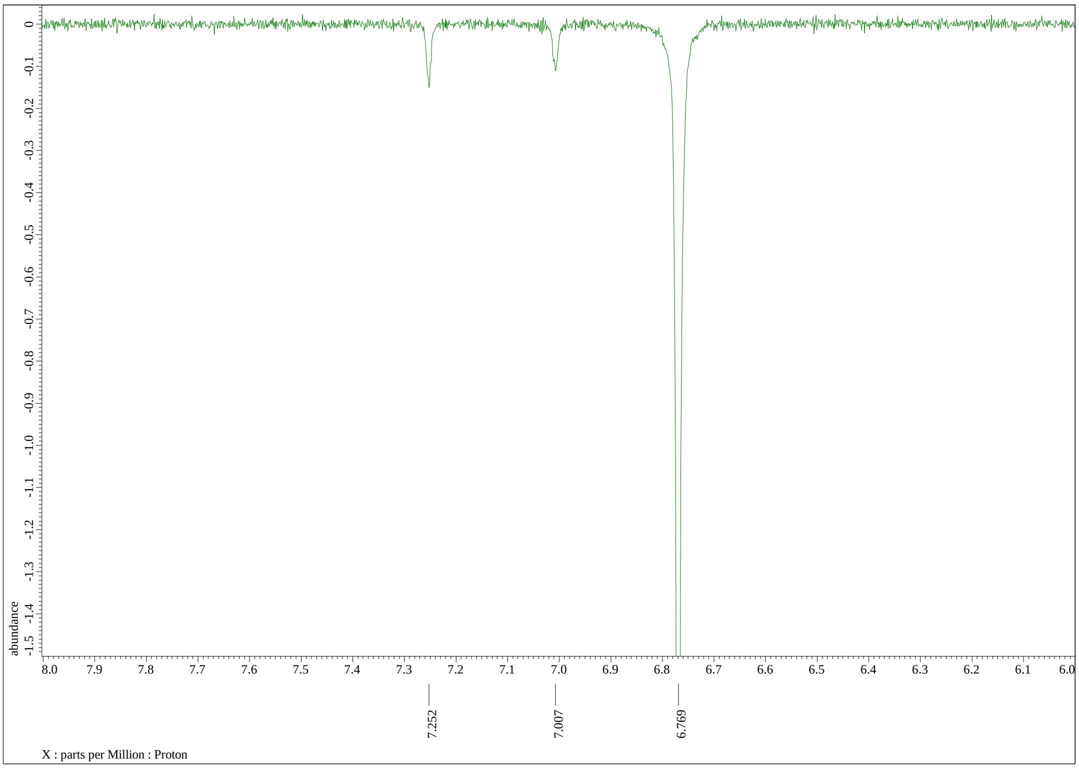


Fig. S31 1D-NOE ($CDCl_3$) spectrum of **cylindrical macrocycle 1a**–(*PM*).

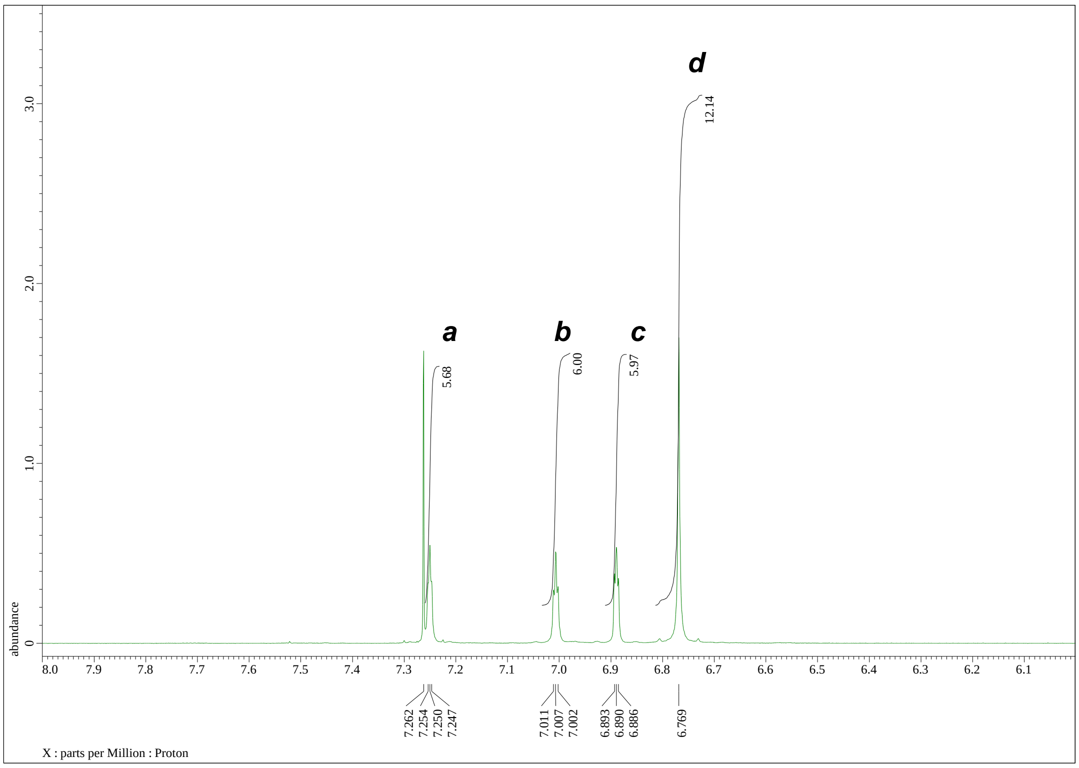
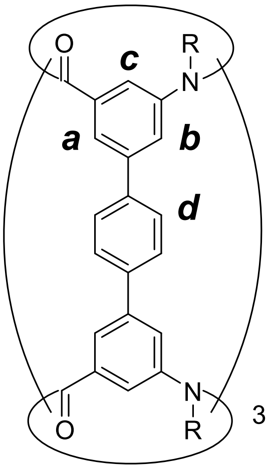


Fig. S32 The magnified chart of the aromatic region of ^{1}H NMR (400 MHz, CDCl$_3$) spectrum of **cylindrical macrocycle 1a**–(*PM*).



$R = C_{10}H_{21}$

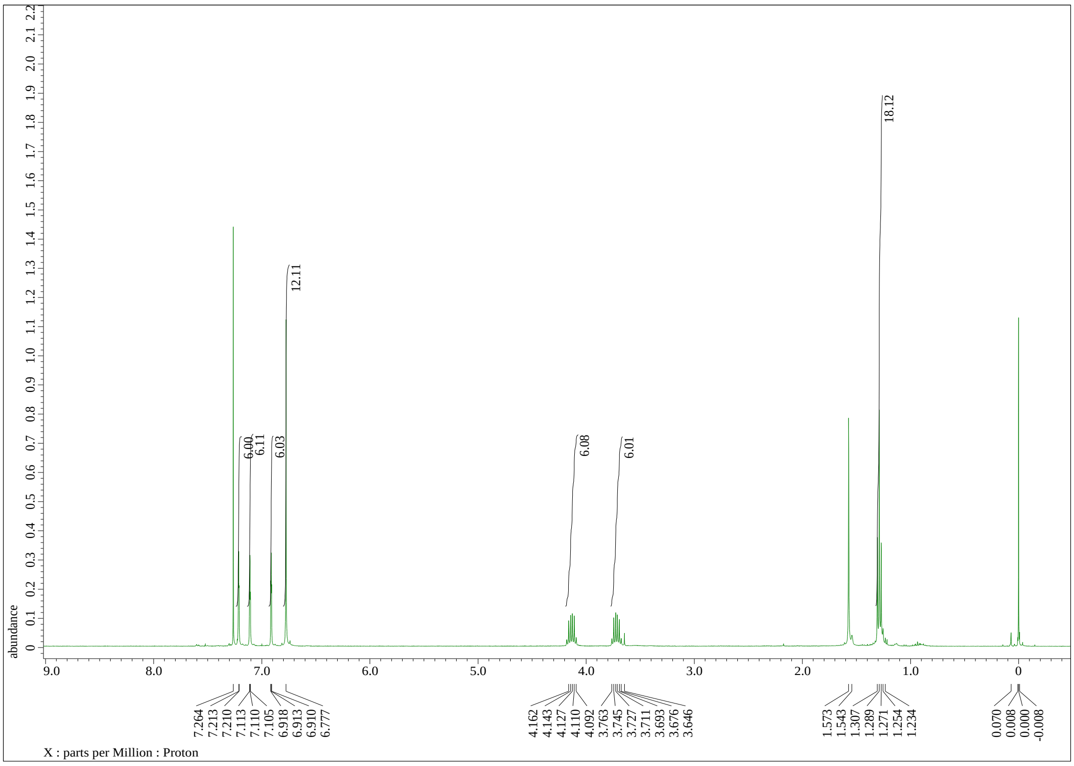


Fig. S33 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **cylindrical macrocycle 1b**–(*PP*).

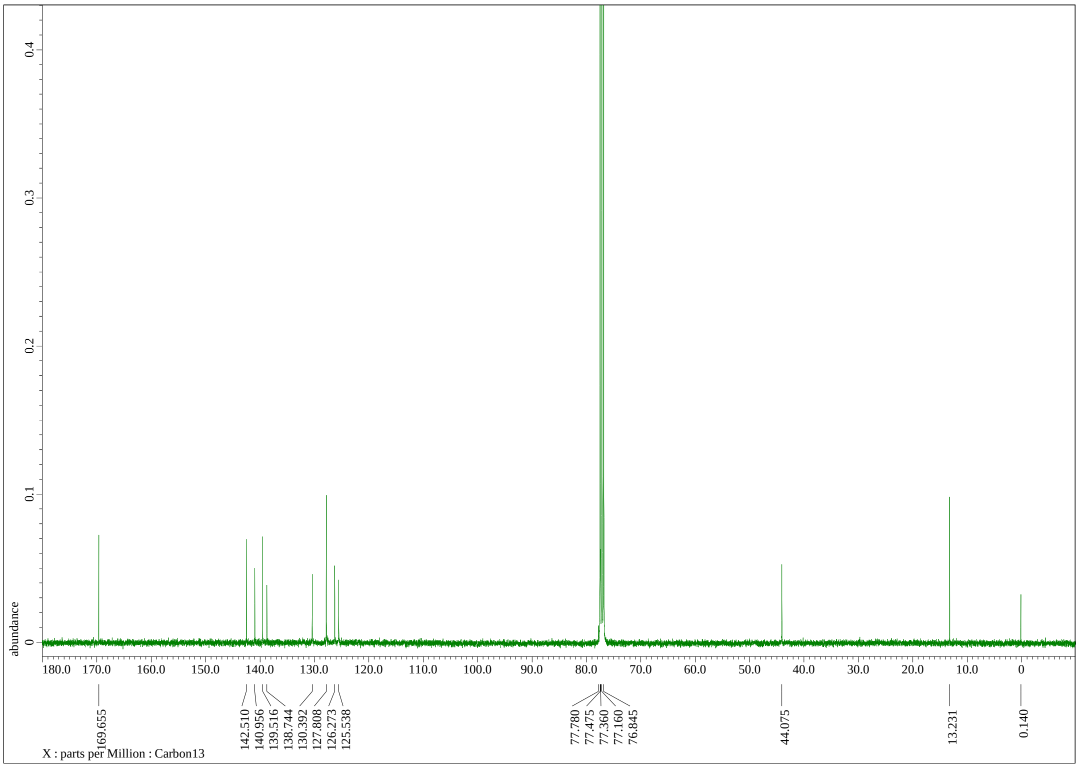


Fig. S34 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **cylindrical macrocycle 1b**–(*PP*).

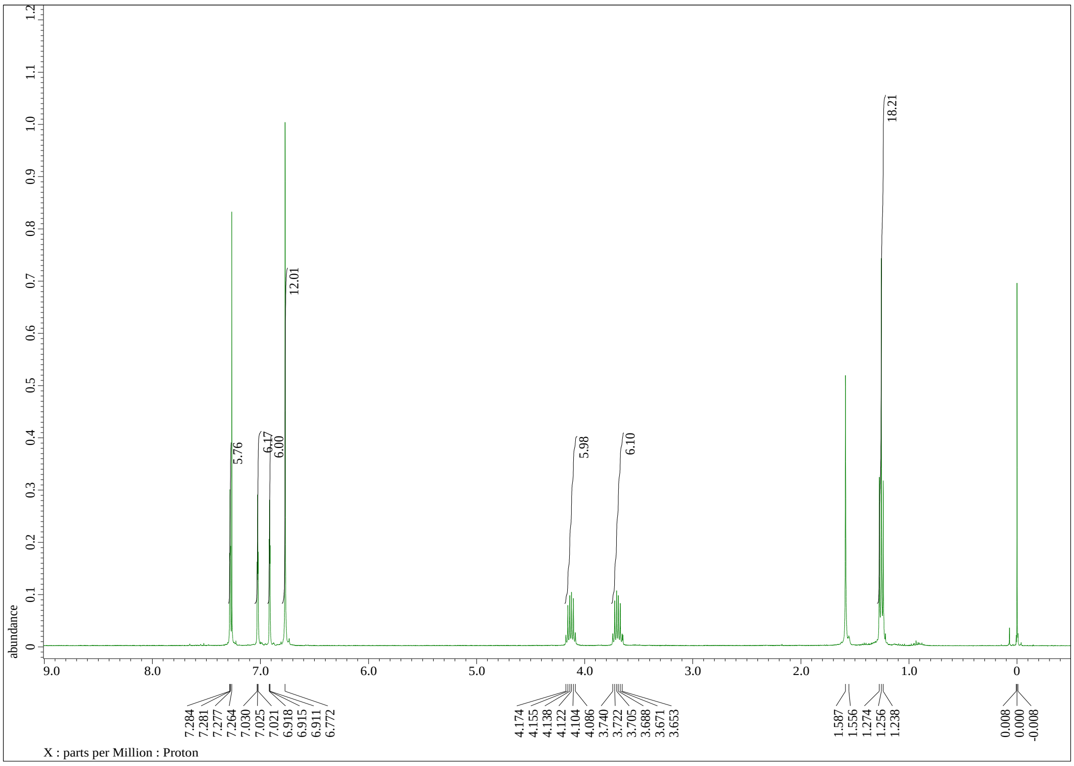


Fig. S35 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **cylindrical macrocycle 1b**–(*PM*).

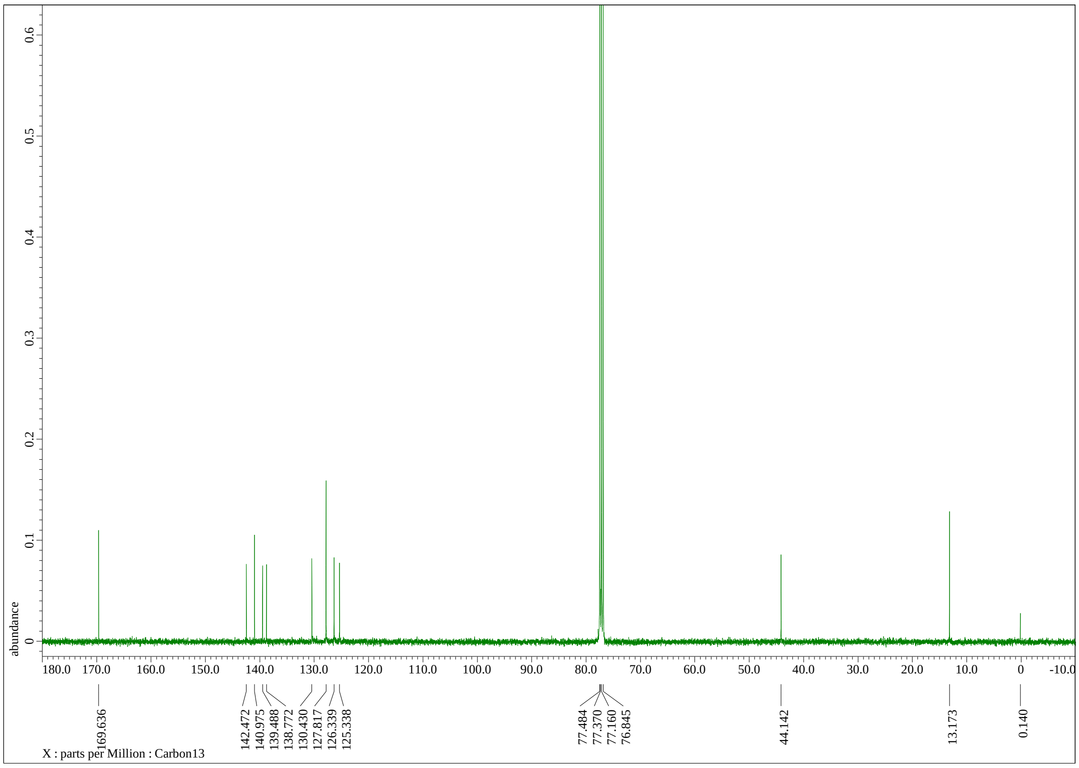
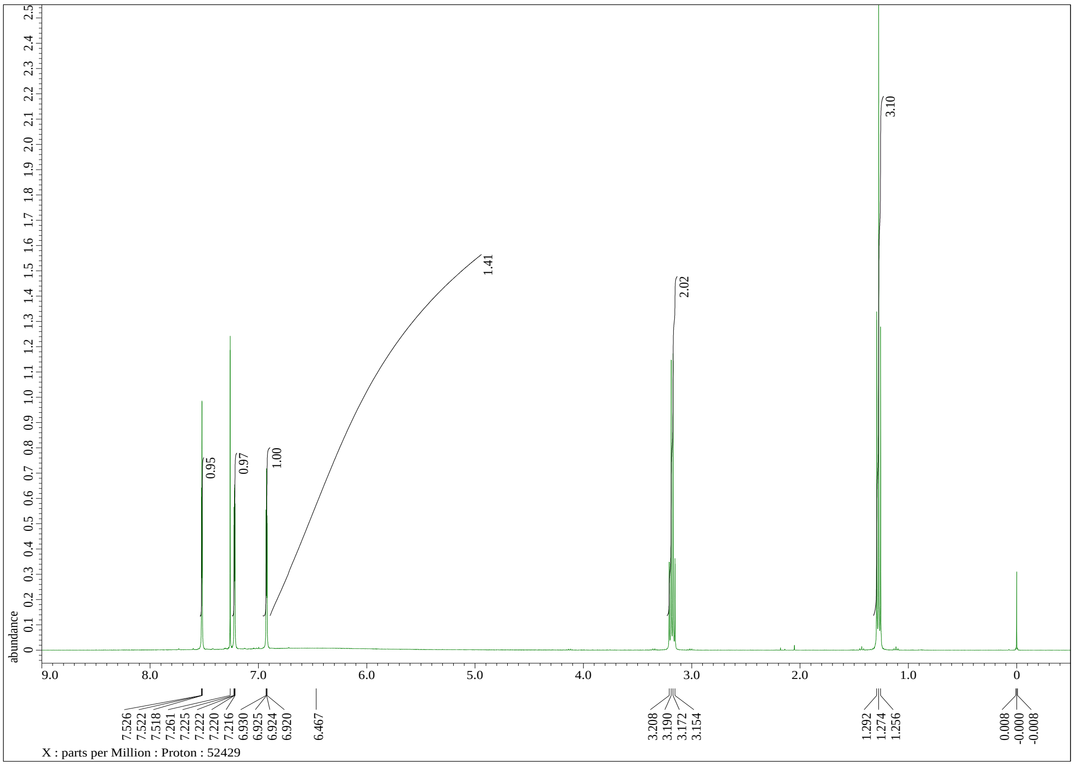


Fig. S36 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **cylindrical macrocycle 1b**–(*PM*).



Fig, S37 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3-bromo-5-(ethylamino)benzoic acid (9b)**.

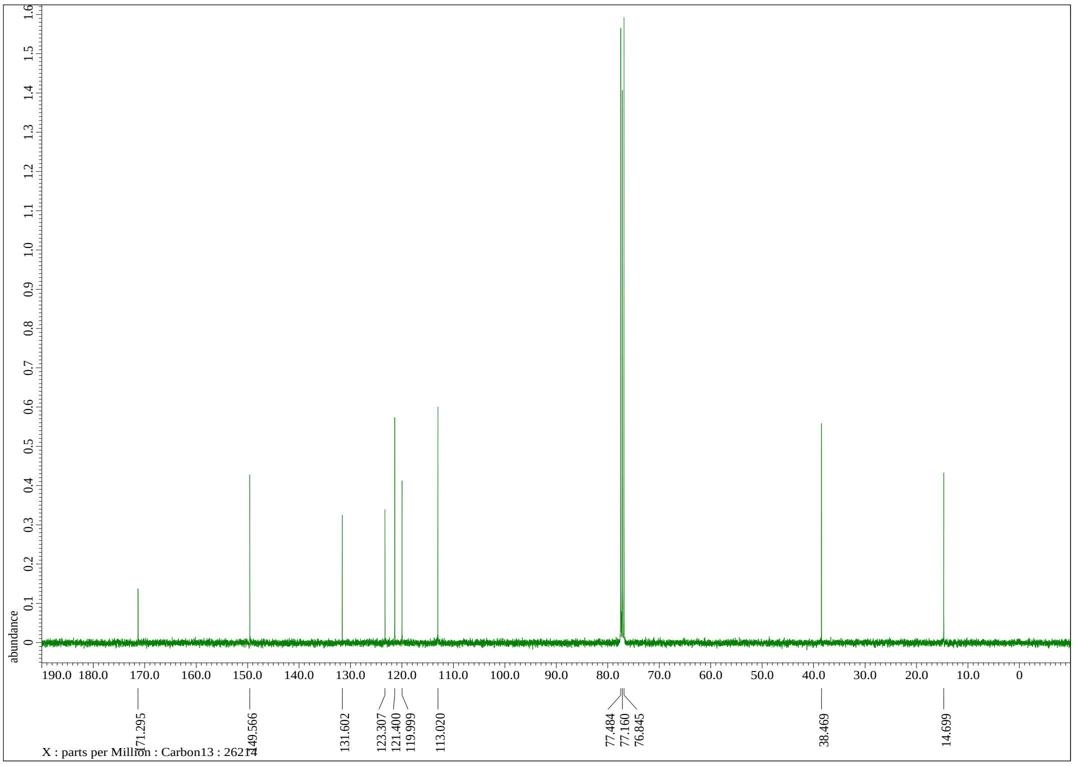


Fig. S38 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3-bromo-5-(ethylamino)benzoic acid (9b)**.

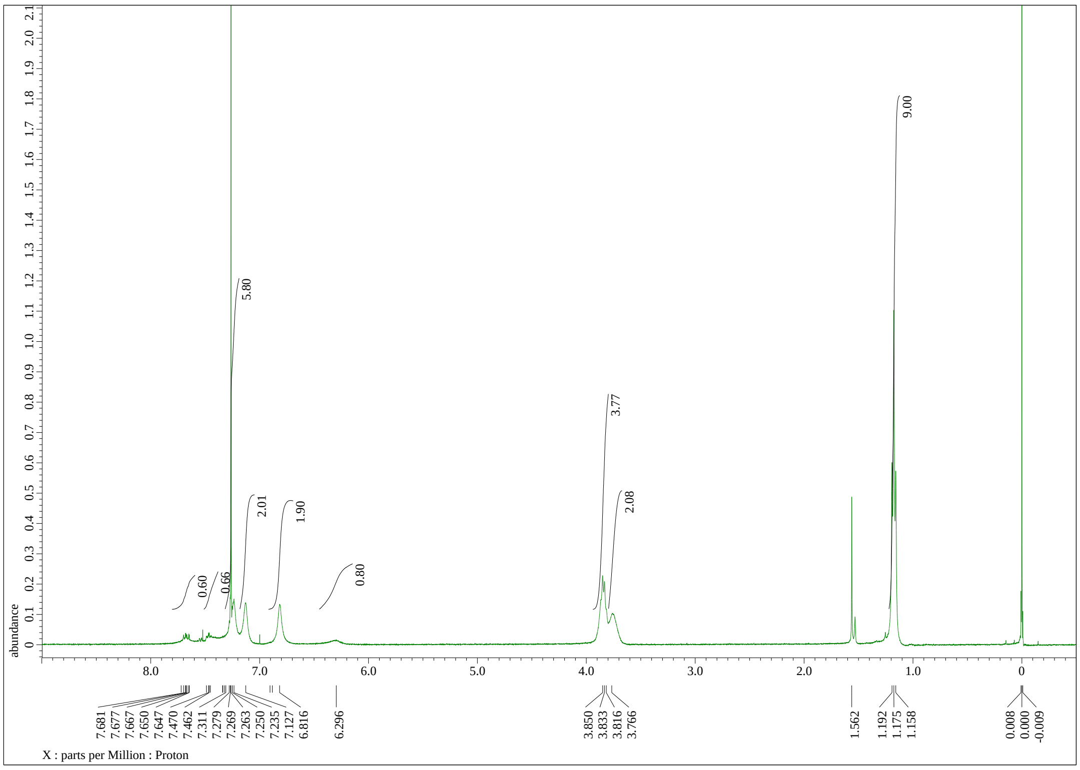


Fig. S39 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **calix[3]aramide 10b**.

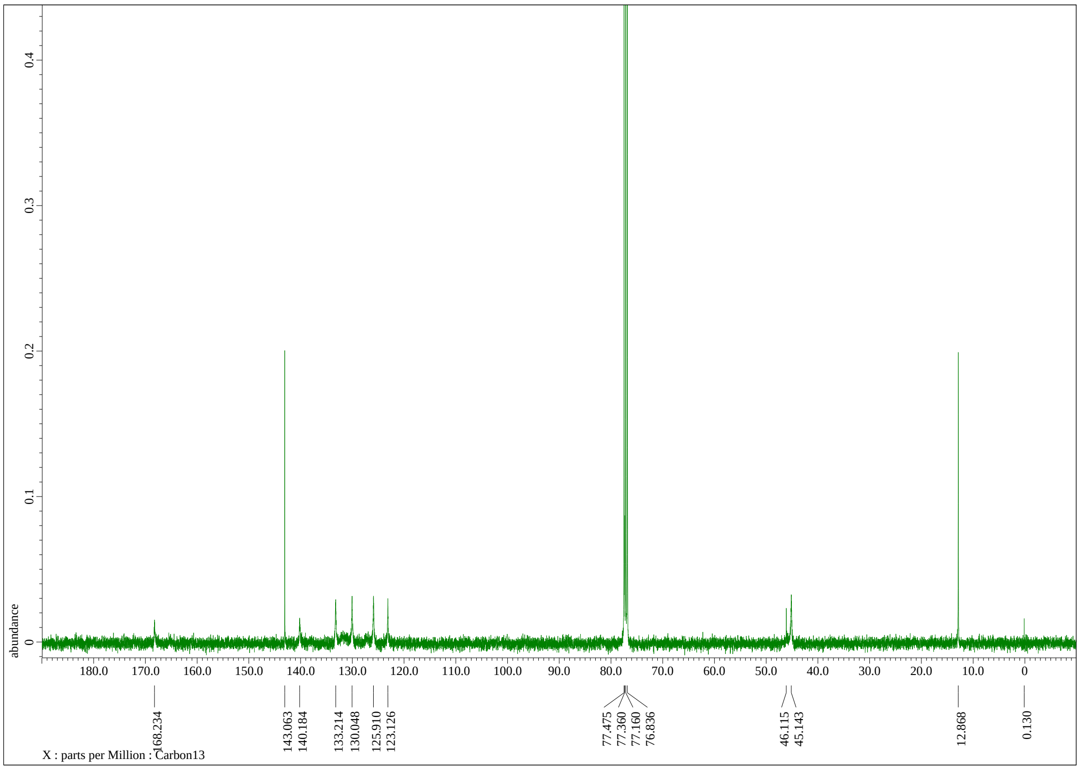


Fig. S40 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **calix[3]aramide 10b**.

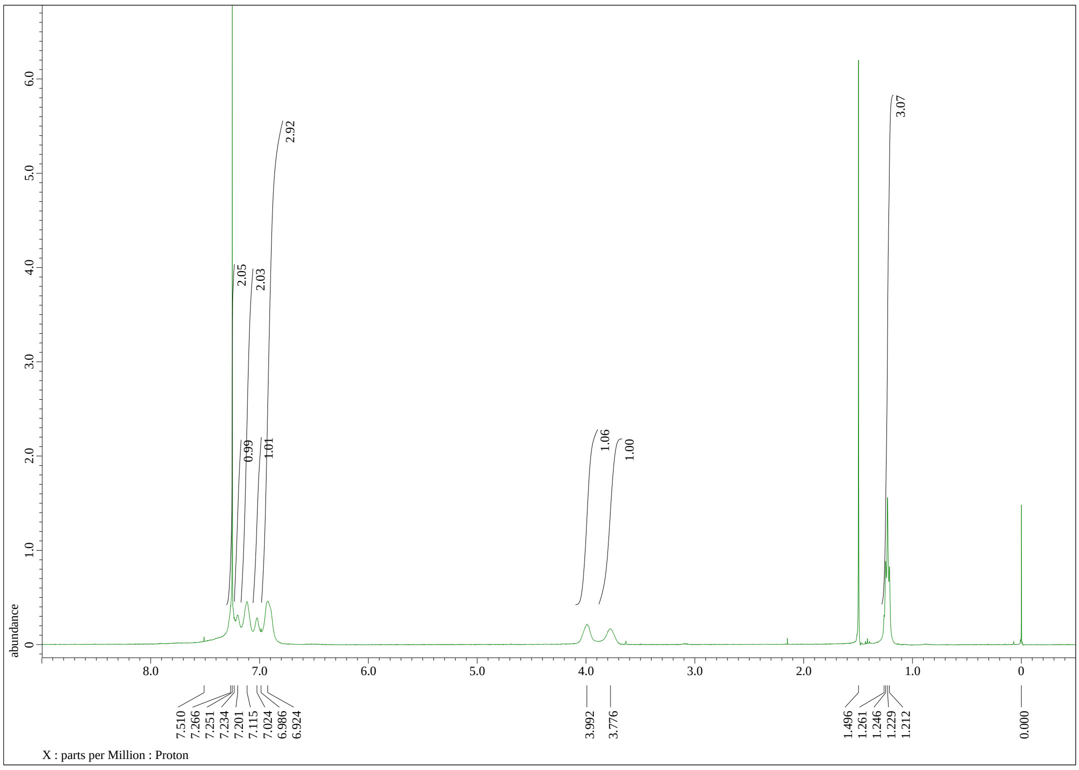


Fig. S41 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **calix[3]aramide 11b**.

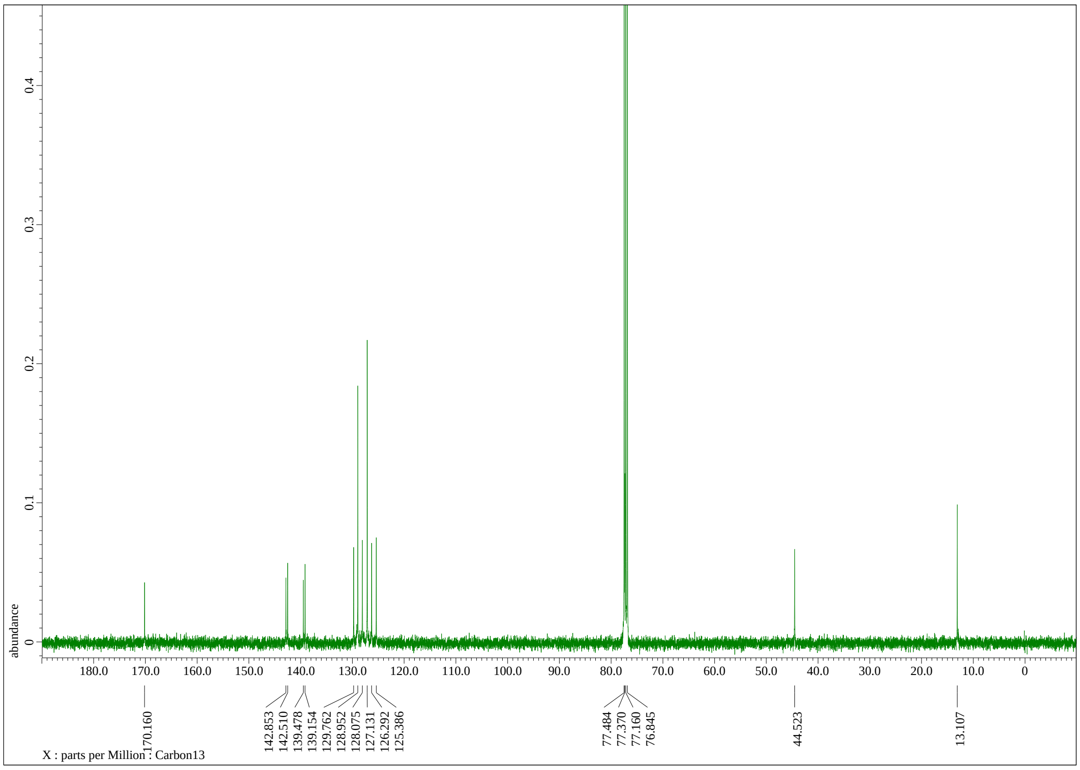


Fig. S42 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **calix[3]aramide 11b**.

GPC chart

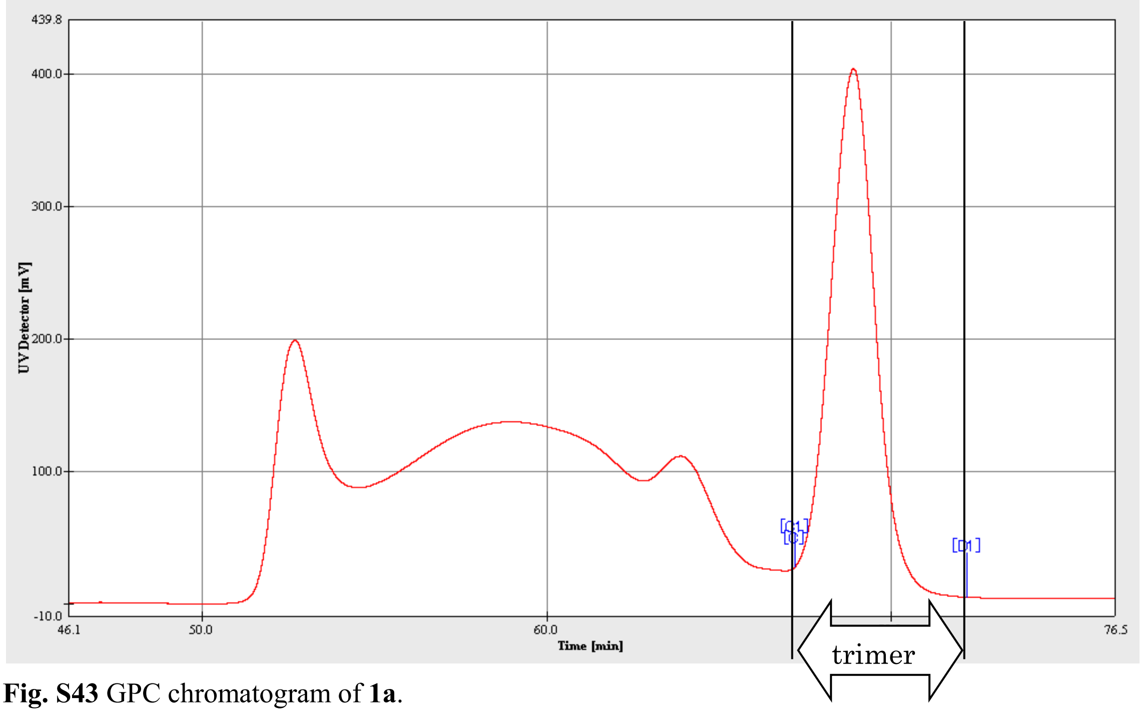


Fig. S43 GPC chromatogram of **1a**.

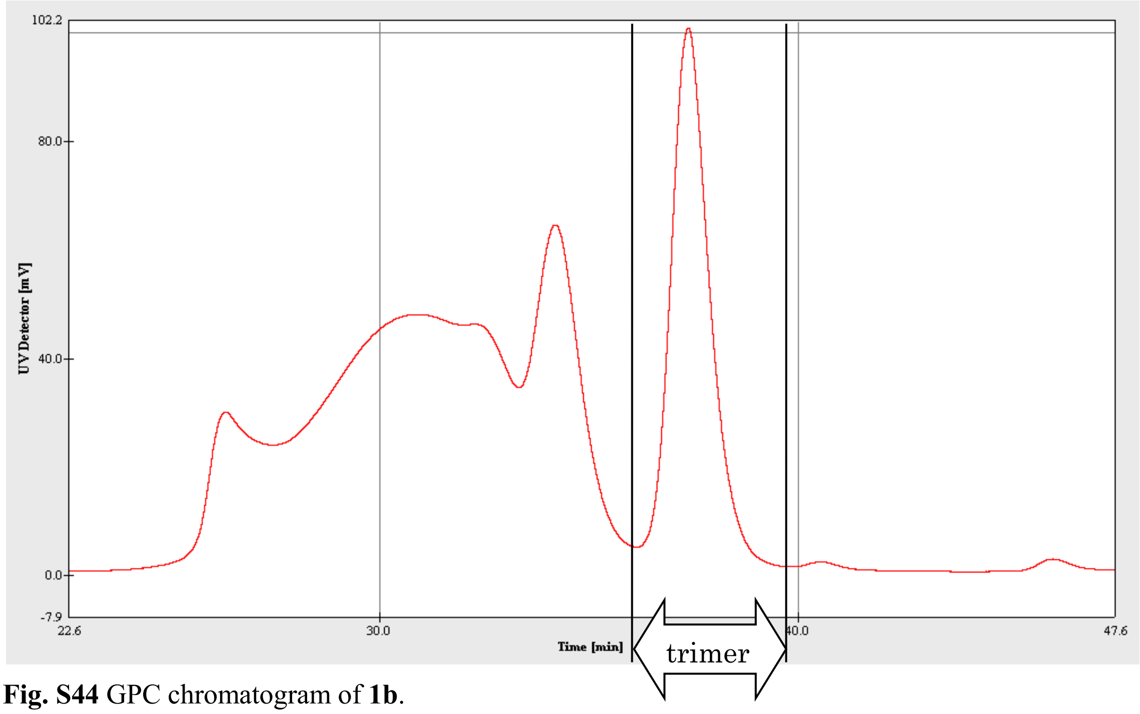


Fig. S44 GPC chromatogram of **1b**.

MS spectra chart

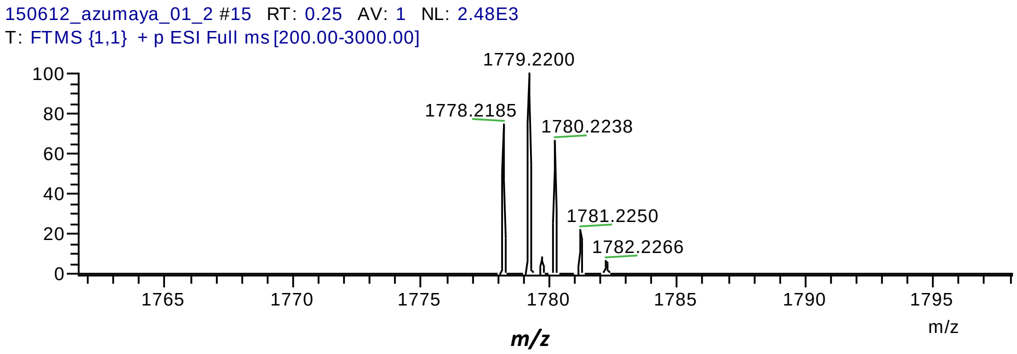


Fig. S45 ESI-MS of cyclic amide trimer **1a**.

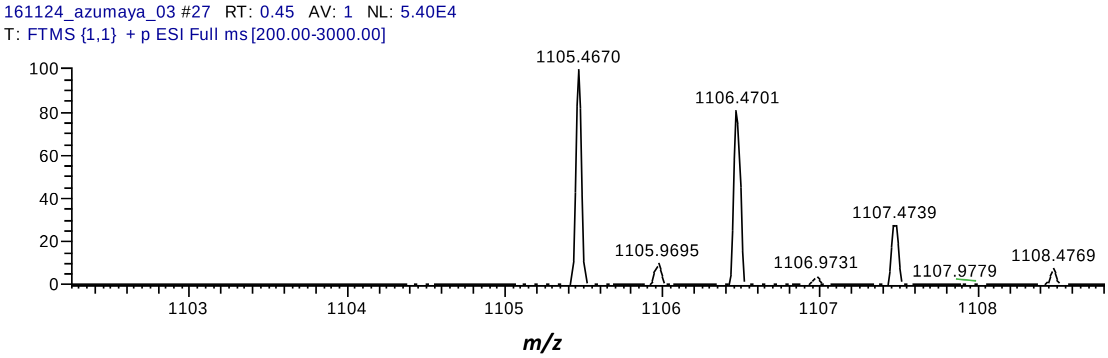


Fig. S46 ESI-MS of cyclic amide trimer **1b**.

Chiral HPLC chart

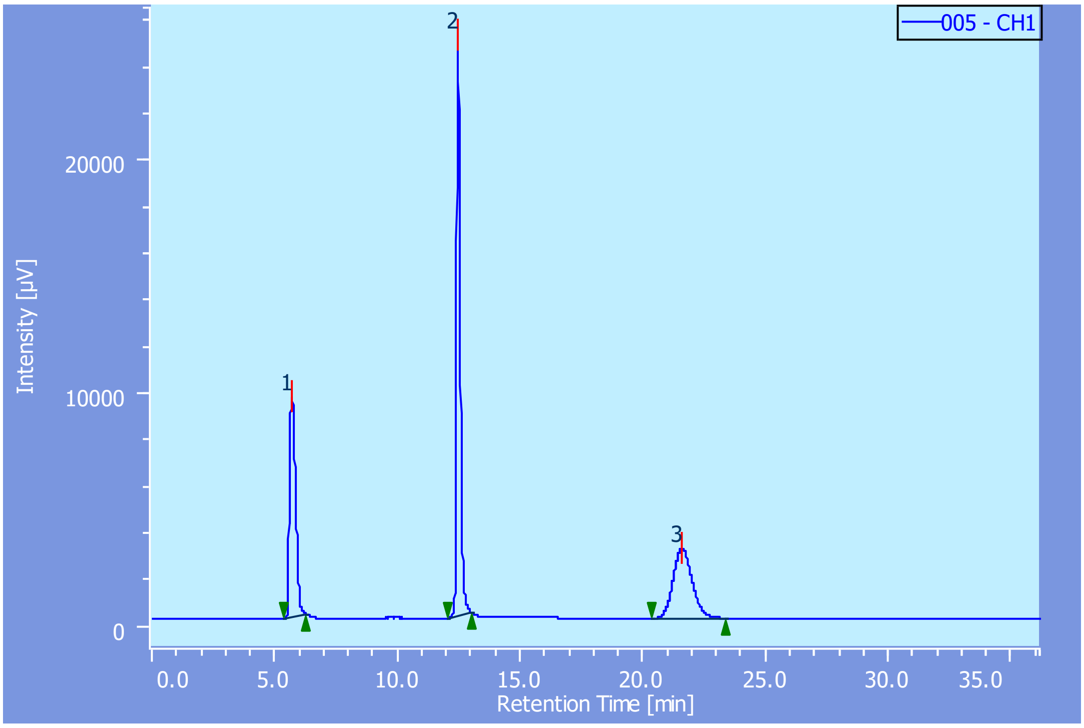


Fig. S47 Chiral HPLC chromatogram of diastereomeric mixture of cyclic amide trimer **1a**.

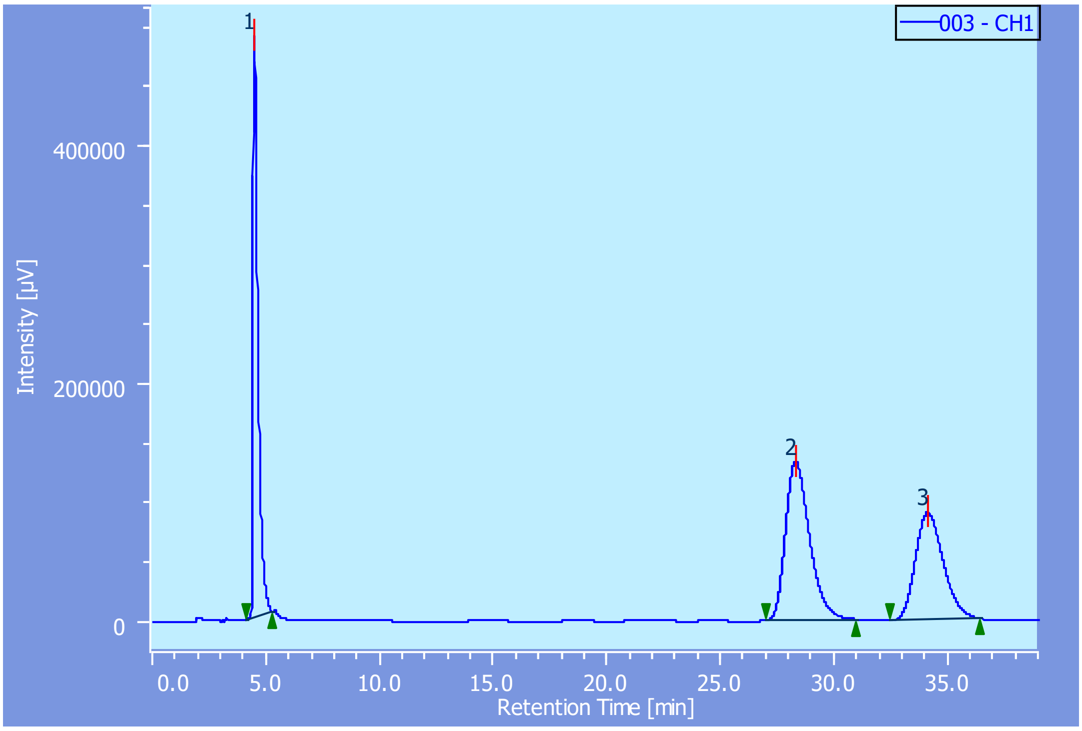


Fig. S48 Chiral HPLC chromatogram of diastereomeric mixture of cyclic amide trimer **1b**.

ECD spectra

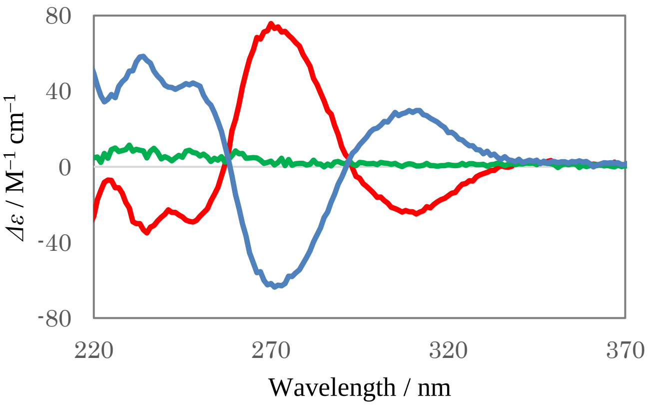


Fig. S49 ECD spectra of cylindrical macrocycle **1b** in ethanol.

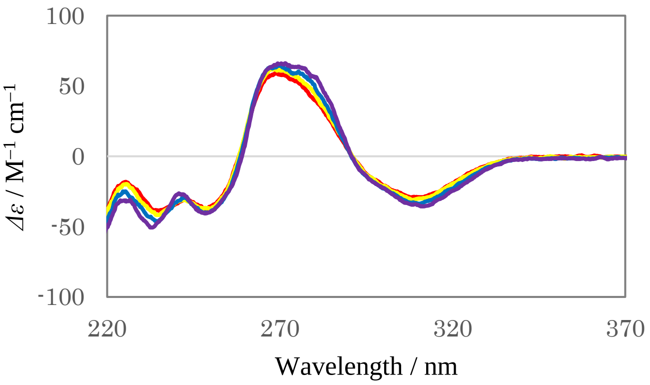


Fig. S50 Temperature dependent ECD spectra of **1a**–(*PP*) in ethanol (red line: 20 °C, yellow line: −10 °C, blue line: −50 °C, purple line: −90 °C).

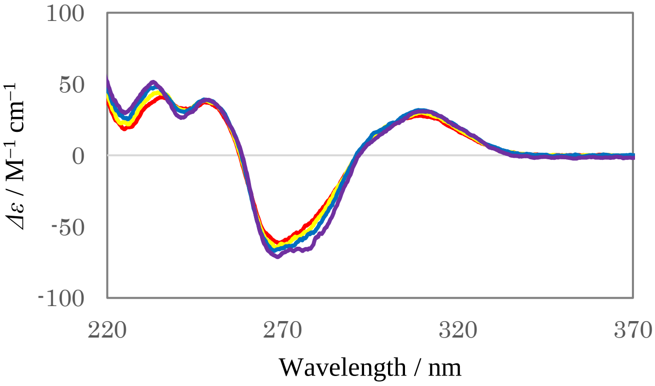


Fig. S51 Temperature dependent ECD spectra of **1a**–(*MM*) in ethanol (red line: 20 °C, yellow line: −10 °C, blue line: −50 °C, purple line: −90 °C).

UV and fluorescence spectra

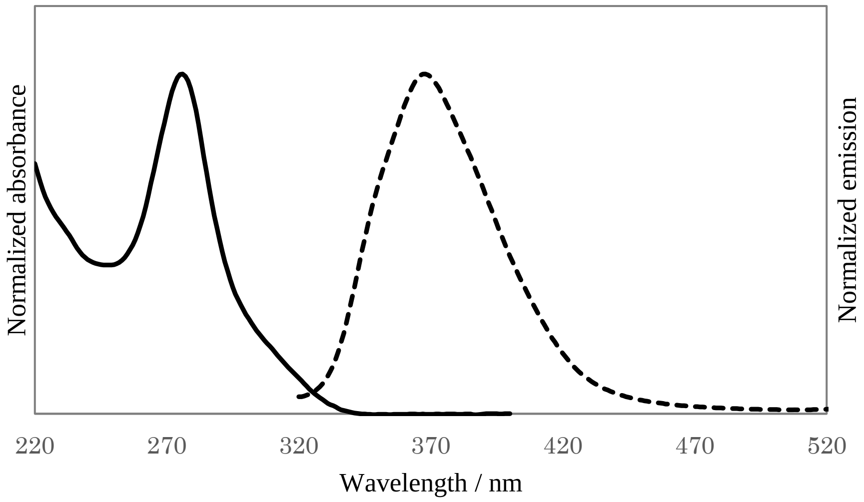


Fig. S52 Normalized absorption (black solid line) and fluorescence spectra (black dotted line) of cylindrical macrocycle **1a** in ethanol solution ($\lambda_{ex} = \lambda_{abs}$, room temperature).

Defined by the sign of the dihedral angle θ of the two C=O groups

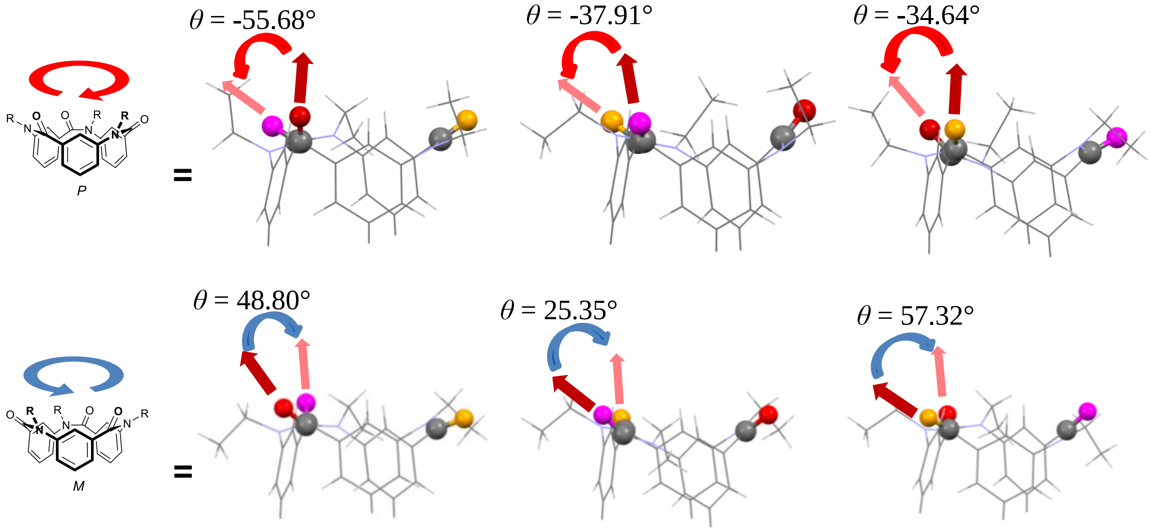


Fig. S53 The illustrative representation of the definition θ (the dihedral angle of two C=O groups) of all angles. Colors: C, gray spheres; O, red, magenta and orange spheres.

4. Dynamic NMR

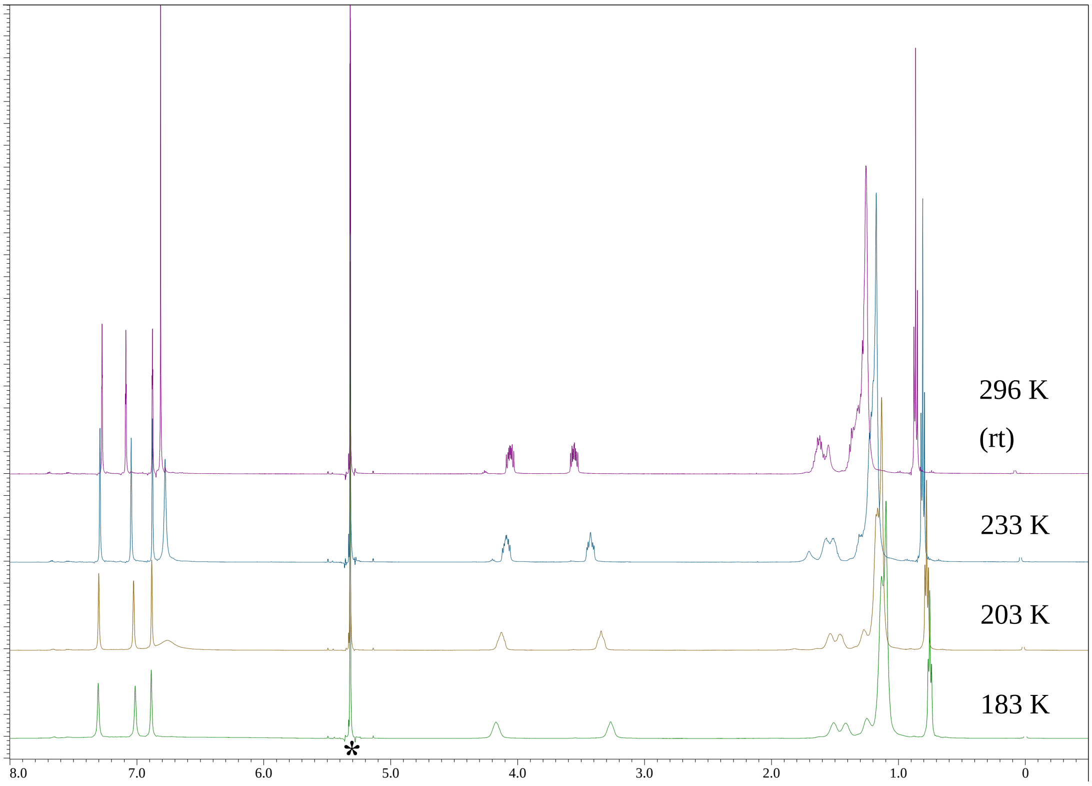


Fig. S54 The temperature dependence of ^{1}H NMR signals of cylindrical macrocycle **1a**–(*PM*) in CD_2Cl_2. Peak marked with an asterisk is the solvent residual signal.

Estimation of rotational barrier

An energy barrier (ΔG) in an equivalent exchange system is calculated according to the equation $\Delta G = -RTc\ln k$, $k = \pi\,\Delta\nu/\sqrt{2}$ (eq. 1).[S2] To calculate this, the coalescence point (Tc) and the difference of chemical shift (Δν) of two exchanged systems are needed. Because the signals of para-phenylene rings were not distinguished even at the lowest (–90 °C) temperature in the measurements, Δν value of the signals of para-phenylene rings were estimated using monomer compound. That is, the chemical shift of Hs on the phenylene rings which were outside of the macrocycle was assumed to be the same as those of **7a** (7.74 ppm) and that of the observed single signal of macrocycle (6.76 ppm) was assumed to be an average of those which were inside and outside of the macrocycle. Accordingly, Δν value was estimated to be 2 x (7.74 ppm – 6.76 ppm) x 500 MHz = 980 Hz. Because those were not distinguished at –90 °C (183 K) then the coalescence point is sure to be below the temperature, if 183 K was assigned to eq. 1, the obtained value (7.73 kcal/mol) must be higher than the real one.

5. Theoretical analysis

Computational details

All computations were performed using the Gaussian 16 package of programs.[S3] Geometry optimizations of **1a**-(*PP*) were executed with the DFT method employing the B3LYP and B97D functionals. The 6-31G(d) basis sets were used for all atoms. The $C_{10}H_{21}$ group was omitted and replaced with a methyl group for these calculations. The UV and ECD spectra were calculated by using the time-dependent DFT method at the B3LYP/6-31G(d), B97D/6-31G(d) or ZINDO/S method. Gaussian band-shape with 2500 cm^{-1} as a half-height width was applied to produce the spectra. The IR and VCD spectra were calculated at the same level as the optimization calculation.

UV and ECD calculation

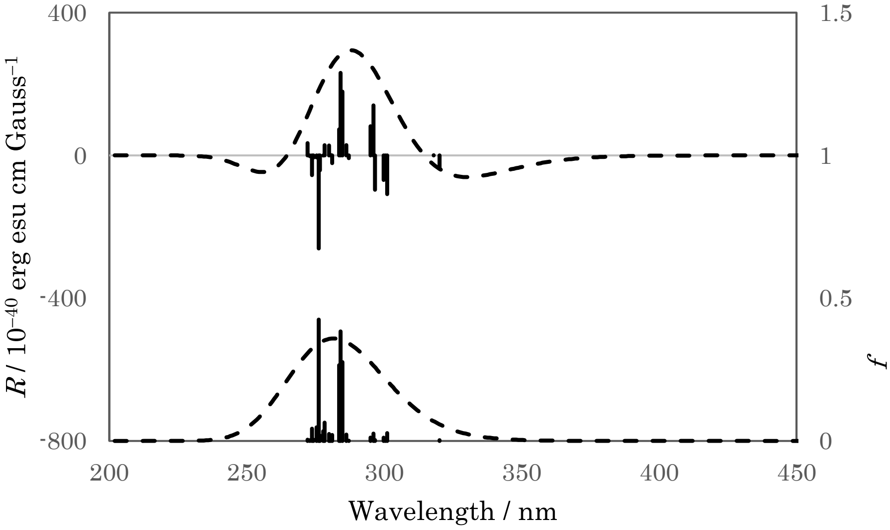


Fig. S55 Stick UV and ECD spectra of **1a**–(*PP*) using TDDFT method (B3LYP/6-31G(d)). Geometry optimization was carried out using B3LYP functional with the 6-31G(d) basis set.

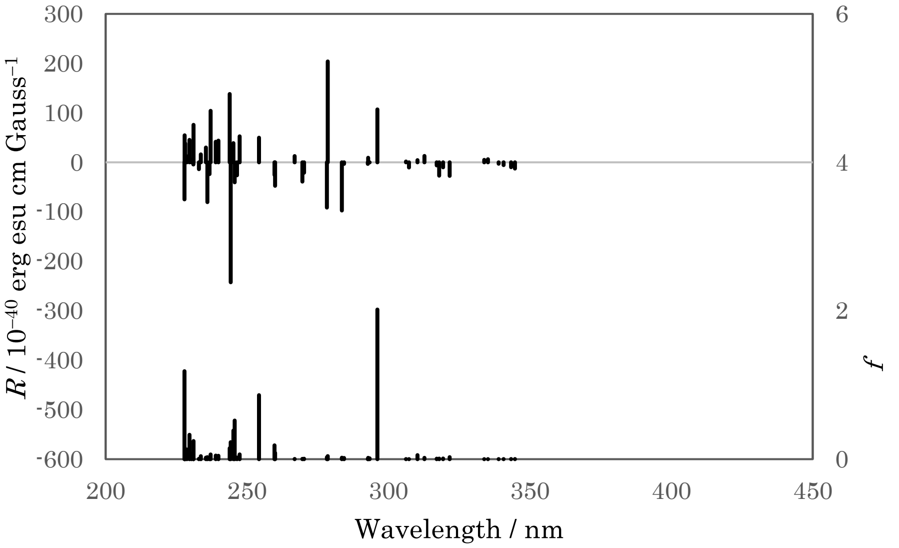


Fig. S56 Stick UV and ECD spectra of **1a**–(*PP*) using ZINDO/S methods. Geometry optimization was carried out using B97D functional with the 6-31G(d) basis set.

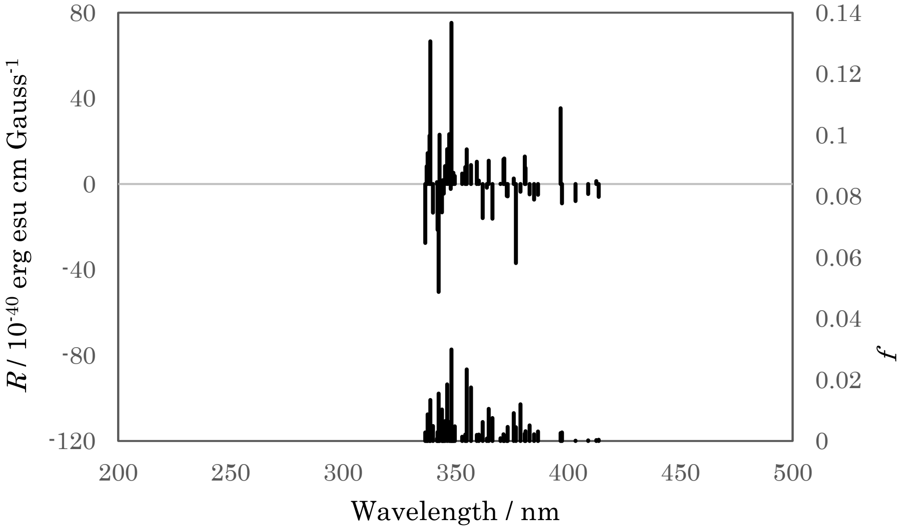
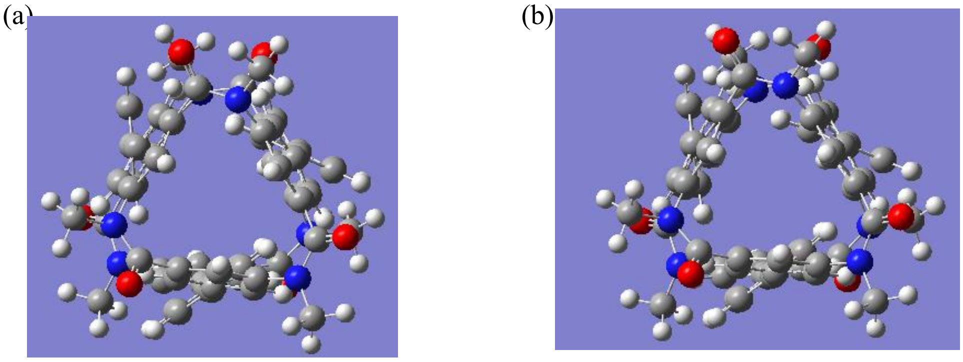
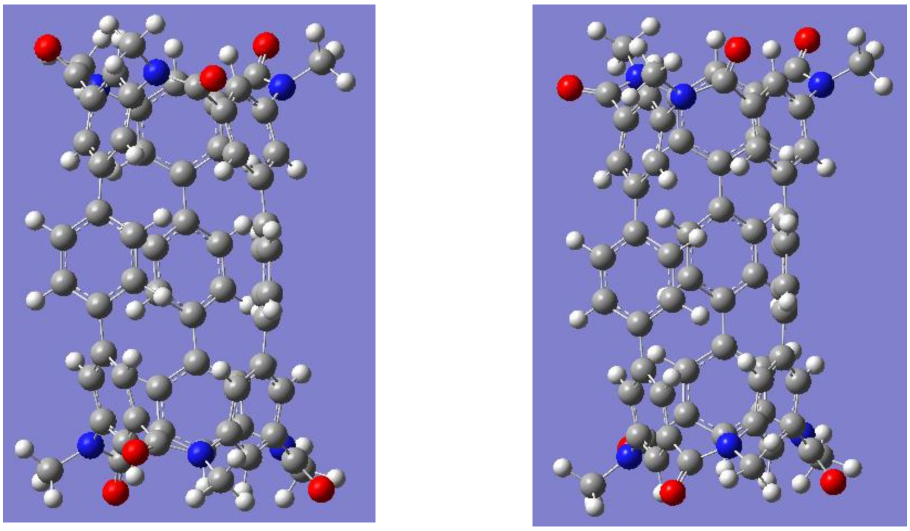


Fig. S57 Stick UV and ECD spectra of **1a**–(*PP*) using TDDFT method (B97D/6-31G(d)). Geometry optimization was carried out using B97D functional with the 6-31G(d) basis set.



Top Top



Side Side

Fig. S58 Energy-minimized structure: (a) **1a**–(*PP*) obtained at the level of B3LYP/6-31G(d). (b) **1a**–(*PP*) obtained at the level of B97D/6-31G(d).

1a–(*PP*) optimized (B3LYP/6-31G(d)).

Sum of electronic and zero-point Energies= -3322.823680 (Hartree/particle)

Sum of electronic and thermal Free Energies= -3322.919485 (Hartree/particle)

No imaginary frequencies

Cartesian coordinate:

C	5.30755700	1.13921300	2.03753800
C	2.55704600	1.50443500	2.50919500
C	4.59353300	0.19996900	2.79037300
C	4.66544600	2.28740600	1.56149700
C	3.30611000	2.47175700	1.81935800
C	3.23176800	0.39044000	3.03456400

C	1.07363700	1.58782100	2.54264500
C	-1.76969500	1.53288400	2.38754300
C	0.29522500	1.16917500	3.63583300
C	0.39786200	2.00720500	1.38429500
C	-0.98742700	1.97815100	1.30864800
C	-1.09870700	1.14455200	3.56089600
C	-3.24103100	1.42144200	2.21416600
C	-5.99201600	1.11478900	1.65112500
C	-3.97035500	0.34799600	2.74662400
C	-3.92315000	2.34071400	1.40278600
C	-5.27376500	2.17494800	1.09121100
C	-5.33226600	0.19034400	2.46602400
C	5.45391200	3.37356700	0.85945600
C	-6.10197200	-0.98280600	3.02848200
O	5.73044100	4.41303200	1.44443900
O	-6.98381300	-0.82316000	3.86238100
N	5.27458200	-0.95377800	3.32162500
N	-5.90455400	3.10017700	0.19397800
C	5.96147500	-0.76063700	4.60394300
C	-6.75926100	4.13653800	0.78332500
C	-5.29578600	1.03929300	-2.08618300
C	-2.54450200	1.30633300	-2.62971000
C	-4.61642300	0.02990500	-2.77737800
C	-4.61993700	2.20717400	-1.71676300
C	-3.26046500	2.34542600	-2.01346700
C	-3.25766900	0.17171100	-3.05298300
C	-1.06022300	1.32662600	-2.70583600
C	1.78342000	1.29278800	-2.54340300
C	-0.35419400	0.13141300	-2.48641800
C	-0.30907200	2.50247600	-2.88023200
C	1.08423700	2.48596200	-2.79866500
C	1.03146600	0.11447200	-2.41022500
C	3.25195800	1.24149300	-2.32463800
C	5.99572400	1.00994600	-1.70257100
C	3.99863300	0.13055400	-2.74448300
C	3.90994700	2.23705300	-1.58731800

C	5.26119000	2.10996700	-1.25073200
C	5.35531200	0.00612100	-2.43395000
C	-5.37834200	3.34375000	-1.06513500
C	6.13011200	-1.20603200	-2.89416900
O	-5.56988700	4.39254400	-1.66655600
O	7.07546700	-1.10907000	-3.66494500
N	-5.32771500	-1.13532900	-3.23615100
N	5.88463400	3.10605800	-0.42725100
C	-6.02533100	-1.00320300	-4.51985000
C	5.66370100	-2.26232700	0.01246500
C	2.88941100	-2.76282000	0.07867400
C	4.96558000	-2.50984800	-1.17165300
C	4.97773300	-2.22441300	1.22943300
C	3.60719800	-2.48557700	1.25454700
C	3.59618200	-2.78784300	-1.13502000
C	1.40821800	-2.88260100	0.12165400
C	-1.44020000	-2.87955600	0.14866300
C	0.67187800	-3.67093700	-0.78046000
C	0.68528000	-2.11680000	1.05248200
C	-0.70250600	-2.11956000	1.07056300
C	-0.72421500	-3.66539500	-0.77107900
C	-2.92069000	-2.75234800	0.12982800
C	-5.68929400	-2.24337500	0.11545600
C	-3.61308500	-2.57253300	-1.07790300
C	-3.64322800	-2.66958000	1.33051800
C	-5.01039600	-2.39003100	1.32713700
C	-4.98582700	-2.30847900	-1.09094300
C	5.74589200	-1.96880000	2.50117800
C	-5.74918200	-2.13965200	-2.38090700
O	6.70616300	-2.66503200	2.80629900
O	-6.67758200	-2.88962300	-2.65796200
N	5.66272500	-2.42856700	-2.42932200
N	-5.72174000	-2.23307700	2.56813100
C	6.34418700	-3.64049000	-2.89304800
C	-6.41326900	-3.41050200	3.09883200
C	6.73317700	4.09881300	-1.09320800

H	6.36263000	0.97604300	1.83794300
H	2.81511000	3.37218800	1.46306900
H	2.68535800	-0.37044600	3.58360700
H	0.78240800	0.87081800	4.56057500
H	0.96509200	2.29143100	0.50386500
H	-1.46496000	2.23781000	0.37010100
H	-1.67151900	0.83221900	4.43012300
H	-3.46390700	-0.39810700	3.35070100
H	-3.39549800	3.19766900	0.99770700
H	-7.04488700	0.98681600	1.41849100
H	6.26675900	-1.73423100	4.98795000
H	6.85566700	-0.13311700	4.49534900
H	-7.33225400	4.61337800	-0.01215300
H	-7.43426000	3.67227200	1.50644700
H	-6.34884900	0.91720100	-1.85108900
H	-2.74198800	3.24804600	-1.70354200
H	-2.74766700	-0.62312600	-3.58732800
H	-0.89646600	-0.78906200	-2.29779100
H	-0.81627400	3.44046600	-3.09016100
H	1.63521700	3.41097400	-2.94725500
H	1.53146500	-0.81696500	-2.16820800
H	3.51555600	-0.64958200	-3.32304700
H	3.35605000	3.09575600	-1.22104300
H	7.04693700	0.91639100	-1.44742800
H	-6.89869200	-0.34309700	-4.43886000
H	-6.36380300	-1.99033200	-4.83463000
H	6.73207600	-2.07090900	-0.01515200
H	3.08925000	-2.48121400	2.20667700
H	3.07240300	-2.95373000	-2.07153800
H	1.19340100	-4.30670300	-1.49113300
H	1.21216700	-1.45356000	1.72926500
H	-1.21983600	-1.46607300	1.76546700
H	-1.26396100	-4.29222700	-1.47624300
H	-3.06650200	-2.60292700	-2.01471500
H	-3.13435700	-2.79715500	2.28086400
H	7.20254200	-3.89149300	-2.25624700

H	5.63790800	-4.47510100	-2.87759400
H	-6.81052100	-3.15989800	4.08243800
H	-7.24362800	-3.71484200	2.44870500
H	7.43973100	3.58711400	-1.75222200
H	7.27001200	4.66229800	-0.33023200
H	-5.33556500	-0.58614700	-5.25845100
H	-6.16464200	4.90450700	1.29464000
H	-5.70596000	-4.24133500	3.17701800
H	5.27393800	-0.27803800	5.30331400
H	6.70246400	-3.47028900	-3.90851700
H	6.13443200	4.79708800	-1.69206900
H	-6.75757700	-2.04955900	0.11025000

1a–(*PP*) optimized (B97D/6-31G(d)).

Sum of electronic and zero-point Energies= -3320.541354 (Hartree/particle)

Sum of electronic and thermal Free Energies= -3320.636023 (Hartree/particle)

No imaginary frequencies

Cartesian coordinate:

C	5.29939000	1.02182800	2.12672700
C	2.50541800	1.26526200	2.45839500
C	4.57440700	0.01293900	2.78279900
C	4.64219400	2.18567000	1.69336800
C	3.25625400	2.30425400	1.86846700
C	3.19193000	0.14207100	2.96624600
C	1.02298100	1.30268400	2.44120100
C	-1.82280500	1.26536700	2.27477000
C	0.24103700	0.79756100	3.50392400
C	0.35578400	1.78294600	1.29207300
C	-1.03650200	1.76249100	1.21148900
C	-1.15706200	0.78242400	3.42410300
C	-3.29711900	1.20903100	2.13331900
C	-6.09404600	1.03134300	1.67804500
C	-4.04886000	0.14070700	2.65814300
C	-3.97689800	2.19338400	1.38990800
C	-5.35211500	2.09184800	1.13352100
C	-5.43217200	0.04683800	2.42868000

C	5.45474600	3.32741300	1.10898200
C	-6.20658400	-1.14872400	2.93615000
O	5.69186100	4.33910200	1.76908000
O	-7.15329100	-1.03644200	3.71487400
N	5.27029000	-1.15871900	3.25560500
N	-5.97643500	3.07479600	0.29773400
C	5.94911200	-1.00378000	4.55210600
C	-6.89013300	4.02899400	0.94479900
C	-5.29774100	1.15316400	-2.06178500
C	-2.50010200	1.38841600	-2.40166100
C	-4.58388000	0.15922300	-2.75143700
C	-4.62799600	2.30015000	-1.60371100
C	-3.24337000	2.42368000	-1.79556300
C	-3.20160700	0.28039300	-2.92571600
C	-1.01665800	1.40022100	-2.39879300
C	1.83070100	1.36411900	-2.23454900
C	-0.30945300	0.18591000	-2.24400200
C	-0.26995200	2.59831400	-2.46689600
C	1.12759000	2.58112300	-2.38196900
C	1.08330200	0.16834700	-2.17135200
C	3.30383400	1.31656300	-2.07951800
C	6.09587000	1.11868700	-1.61557700
C	4.05429100	0.25184700	-2.61419500
C	3.97929000	2.28673600	-1.31577200
C	5.35279900	2.16816100	-1.05170300
C	5.43689100	0.14962300	-2.38827100
C	-5.42413500	3.40563400	-0.93665400
C	6.21199000	-1.01922800	-2.95410700
O	-5.62583400	4.48029600	-1.50202800
O	7.18245000	-0.86742800	-3.69562500
N	-5.29141500	-0.97419400	-3.29491600
N	5.97243200	3.10509000	-0.16176800
C	-5.97444700	-0.72949600	-4.57525500
C	5.70952000	-2.25389500	-0.15652100
C	2.89994100	-2.61815300	-0.11700000
C	4.99701500	-2.41355700	-1.35380400

C	5.01965600	-2.24630300	1.06595700
C	3.63061400	-2.43711600	1.07655800
C	3.61068700	-2.62437400	-1.33637900
C	1.41834300	-2.68743900	-0.08038300
C	-1.43366400	-2.68672300	-0.02063900
C	0.67117100	-3.39231600	-1.05095800
C	0.70702900	-1.97841100	0.91443500
C	-0.68729600	-1.98381400	0.94967800
C	-0.72906300	-3.38699600	-1.02549900
C	-2.91458900	-2.61389800	-0.00521700
C	-5.71897700	-2.25293000	0.02862100
C	-3.63098400	-2.40575700	-1.20036800
C	-3.62869100	-2.64194900	1.21063600
C	-5.01552100	-2.44295900	1.22688300
C	-5.02109700	-2.21061300	-1.18913600
C	5.79257900	-2.08555100	2.35223600
C	-5.78979100	-1.97846100	-2.46648900
O	6.78463400	-2.77424300	2.59608300
O	-6.76500100	-2.67091900	-2.76308100
N	5.69990200	-2.27136300	-2.60449800
N	-5.72885000	-2.37698200	2.47800100
C	6.37004100	-3.47498200	-3.11649500
C	-6.40567800	-3.60863700	2.90762500
C	6.88828900	4.09417700	-0.74859700
H	6.37099400	0.89714400	1.96545600
H	2.74379300	3.20335500	1.52472500
H	2.63952100	-0.66981900	3.43971600
H	0.73529200	0.43890900	4.40911700
H	0.93459500	2.11479100	0.42977400
H	-1.51996500	2.07623300	0.28750800
H	-1.74347000	0.41554800	4.26875400
H	-3.54672000	-0.65536200	3.20623700
H	-3.42941100	3.04650300	0.99243300
H	-7.16272000	0.94451400	1.47900400
H	6.31472300	-1.98511900	4.87773500
H	6.80534300	-0.31105800	4.47514000

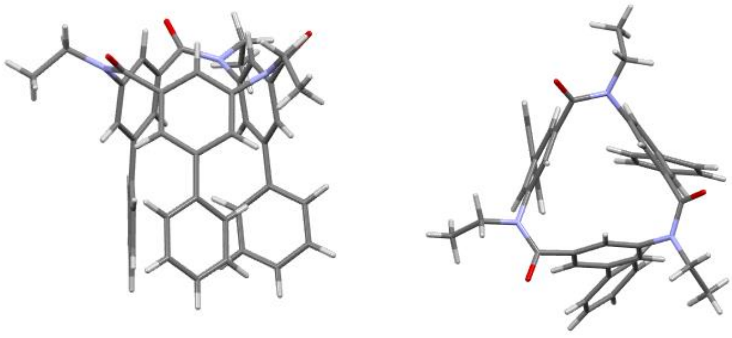
H	-7.43803400	4.57428500	0.16701700
H	-7.58733600	3.47061800	1.58489400
H	-6.36843900	1.03271200	-1.89256000
H	-2.72769000	3.30188800	-1.40501000
H	-2.66268600	-0.50543900	-3.45390800
H	-0.85550100	-0.74849900	-2.11523500
H	-0.78937400	3.54777000	-2.60990100
H	1.68540600	3.51667300	-2.45701100
H	1.59634400	-0.77575600	-1.99596400
H	3.55532600	-0.50975500	-3.21123900
H	3.42362000	3.10719000	-0.86312500
H	7.16328800	1.02727400	-1.41212400
H	-6.82399400	-0.03597700	-4.44826500
H	-6.34998900	-1.68465800	-4.96153000
H	6.78875700	-2.10018000	-0.17847700
H	3.10865700	-2.45100700	2.03070700
H	3.07871200	-2.71169700	-2.28403400
H	1.19361800	-3.96748100	-1.81791000
H	1.24925300	-1.36291100	1.63036600
H	-1.20345900	-1.38273400	1.69785000
H	-1.28718500	-3.95336900	-1.77379600
H	-3.09190000	-2.35303700	-2.14463300
H	-3.09832700	-2.78750600	2.15183400
H	7.19719600	-3.78335100	-2.45324100
H	5.63414400	-4.29023100	-3.17336400
H	-6.82520200	-3.44562700	3.90769700
H	-7.22179200	-3.87603200	2.21377500
H	7.59745000	3.57330600	-1.40750300
H	7.42254500	4.60227600	0.06307900
H	-5.25273600	-0.28733000	-5.27690600
H	-6.33149000	4.75096900	1.56474200
H	-5.67112600	-4.42696800	2.92744100
H	5.22702600	-0.60215100	5.27728000
H	6.77439800	-3.25378700	-4.11167000
H	6.33303400	4.84284900	-1.33935800
H	-6.79878500	-2.10216800	0.04575400

6. X-ray crystallographic structures

X-ray data were collected on a Rigaku XtaLAB P200 diffractometer with multi-layer mirror monochromated Cu*K*α (λ = 1.54187Å) and a hybrid photon counting detector (PILATUS 200K). The crystal structure was solved by direct methods (SHELXT Version 2014/5)[S4] and refined by full-matrix least-squares SHELXL-2014/7.[S5] All non-hydrogen atoms were refined anisotropically. CCDC 1952540 (**1b**), 1952545 (**11b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystallographic data for **1b**: $C_{87}H_{79}N_6O_7$, M_r = 1320.62, 0.180 × 0.100 × 0.040 mm, monoclinic, $P2_1/n$ (no. 14), a = 14.89204(7), b = 17.25623(10), c = 28.41877(13) Å, β = 98.1145(4) °, V = 7229.95(6) Å^3, Z = 4, $D_{\mathrm{calcd.}}$ = 1.213 gcm^{-3}, $2\theta_{\max}$ = 68.249, T = 103 K, 142071 reflections measured, 13221 unique (R_{int} = 0.0393), μ = 0.612 mm^{-1}, $T_{\max}$ = 0.741, $T_{\min}$ = 0.976. The final R_1 and wR_2 were 0.0654 and 0.1884 (all data) for 1060 parameters and 126 restraints. The residual electron densities (peak and hole) were 0.76 and -0.44 eÅ^{-3}. All non-H-atoms were refined anisotropically, and H-atoms were fixed in geometrically estimated positions and refined using the riding model. The carbon atoms (and each connecting hydrogen atoms) of three *para*-phenylene rings of **1b** were treated as disordered, and the occupancy factors of the major components of the disorder refine to 0.78. C72A and C72B (and each connecting hydrogen atoms) are terminal methyl groups of a disordered **1b**. C72A and C72B have about 0.66 and 0.33 of occupancies respectively (total occupancy is 1.0). The crystal lattice contains some solvent molecules. There are some toluene molecules and methanol molecules disordered over two orientations in the asymmetric unit. First toluene molecule is disordered over two orientations, and the occupancy factors were 0.5 respectively. The remaining void space is filled with highly disordered solvent molecules (two toluene molecules and two methanol molecules, which have about 0.5 of occupancies respectively). Overall, the ratio of **1b**/toluene/MeOH in the crystal is 1:2(0.5 ×4):1(0.5×2). The hydrogen atoms of a hydroxyl group of methanol molecule were not determined.

Crystallographic data for **11b**: $C_{45}H_{39}N_3O_3$, M_r = 669.82, 0.170 × 0.060 × 0.060 mm, monoclinic, $P2_1/n$ (no. 14), a = 9.47394(8), b = 19.77494(10), c = 19.02693(13) Å, β = 101.6839(8) °, V = 3490.77(4) Å^3, Z = 4, $D_{\mathrm{calcd.}}$ = 1.274 gcm^{-3}, $2\theta_{\max}$ = 68.249, T = 93 K, 45193 reflections measured, 6325 unique (R_{int} = 0.0658), μ = 0.631 mm^{-1}, $T_{\max}$ = 0.819, $T_{\min}$ = 0.963. The final R_1 and wR_2 were 0.0367 and 0.0963 (all data) for 460 parameters and 0 restraints. The residual electron densities (peak and hole) were 0.16 and -0.21 eÅ^{-3}. All non-H-atoms were refined anisotropically, and H-atoms were fixed in geometrically estimated positions and refined using the riding model.



Side view Top view

Fig. S59 Crystal structure of calix[3]aramide **11b**. C, gray sticks; N, blue sticks; O, red sticks; H, white sticks.

7. References

S1. (*a*) K. Rajesh, M. Somasundaram, R. Saiganesh and K. K. Balasubramanian, *J. Org. Chem.*, 2007, **72**, 5867–5869; (*b*) C. J. Monceaux, C. Hirata-Fukae, P. C.-H. Lam, M. M. Totrov, Y. Matsuoka and P. R. Carlier, *Bioorg. Med. Chem. Lett.*, 2011, **21**, 3992–3996.

S2. Oki, M. Applications of Dynamic NMR Spectroscopy to Organic Chemistry; VCH Publishers: New York, 1985.

S3. Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

S4. G. M. Sheldrick, *Acta Crystallogr.*, 2014, **A70**, C1437.

S5. G. M. Sheldrick, *Acta Crystallogr.*, 2015, **C71**, 3–8.