Supporting Information

ENCAPSULATION OF COFACIAL DIARYLACETYLENE DIMERS USING [*c*2]DAISY CHAIN ROTAXANE STRATEGY

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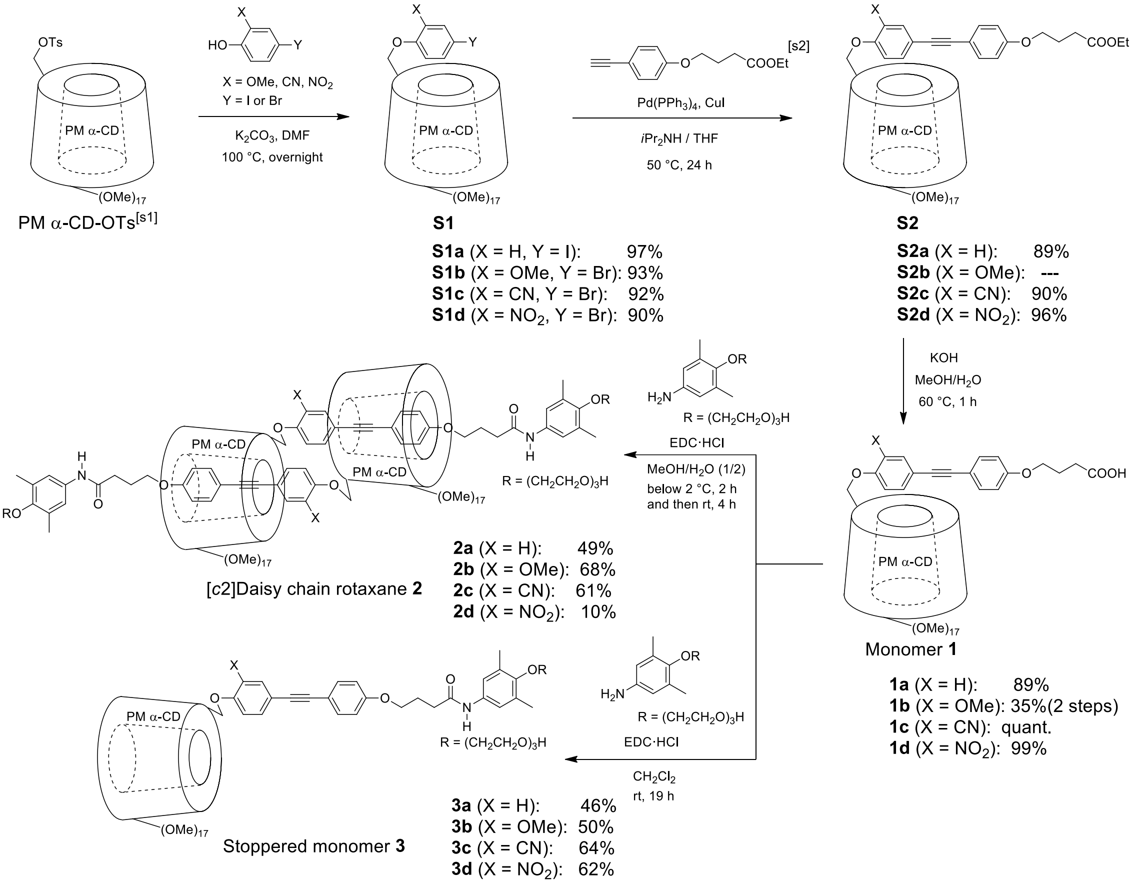
1. General comments

Permethylated α-cyclodextrin monotosylate (PM α-CD-OTs),[s1] Ethyl 4-(4-trimethylsilylethynyl-phenoxy)butyrate[s2] and 4-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}-3,5-dimethylaniline[s2] were prepared by the previous reported procedure. Other reagents were purchased from commercial sources and used without further purification. Commercially available dehydrated DMF was used without further distillation. Melting points were measured with a Stanford Research Systems Optimelt MPA100 melting point apparatus. ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) were recorded by a JEOL JNM-Alice 400 spectrometer. The ^{1}H NMR chemical shifts were reported relative to tetramethylsilane (TMS, 0.00 ppm) or residual protonated solvents (7.26 ppm) in $CDCl_3$ or (3.31 ppm) in CD_3OD. The ^{13}C NMR chemical shifts were reported relative to $^{13}CDCl_3$ (77.0 ppm). Electrospray-ionization time-of-flight high-resolution mass spectrometry (ESI-TOF-HRMS) spectra were recorded on Bruker micrOTOF II-KE02 using sodium trifluoroacetate as cationization reagent. Absorption spectra were recorded by HITACHI U-1900 UV-Vis absorption spectrometer. Fluorescence spectra were recorded by HITACHI FL-7000.

2. Overview for synthetic routes (Scheme S1)



Scheme S1. Overview for synthetic routes of [*c*2]daisy chain rotaxanes **2a**–**d** and stoppered monomers **3a**–**d**.

3. Changes in the chemical shifts of the diarylacetylene protons (Table S1)

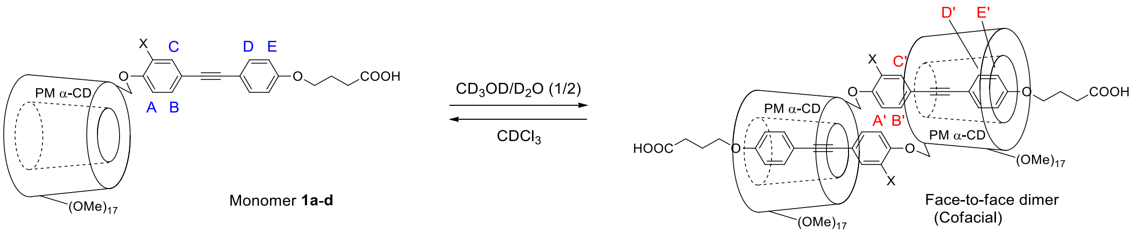
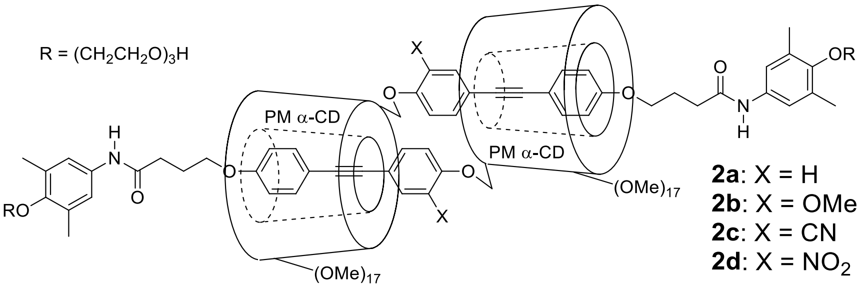


Table S1. Changes in the chemical shifts of the diarylacetylene protons during dimerization.[a]

Monomer	$\Delta\delta$ (ppm)				
	A→A’	B→B’	C→C’	D→D’	E→E’
1a (X = H)	−0.24	−0.05[b]	−0.05[b]	+0.52	+0.19
1b (X = OMe)	−0.39	−0.04	−0.15	+0.54	+0.24
1c (X = CN)	−0.26	−0.01	−0.09	+0.58	+0.24
1d (X = NO_2)	−0.26	+0.02	−0.26	+0.58	+0.23

[a] Values were calculated by subtracting the chemical shifts of protons A–E in $CDCl_3$ from those of the corresponding protons A’–E’ in CD_3OD/D_2O (1/2). [b] Protons B (B’) and C (C’) are equivalent in monomer **1a**.

4. Maximum absorption wavelengths in UV-visible spectra (Table S2)



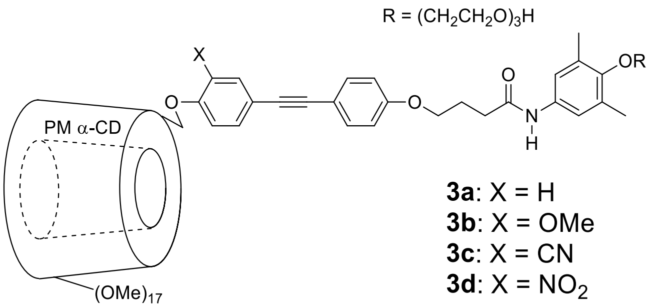
R = $(CH_2CH_2O)_3H$

2a: X = H
2b: X = OMe
2c: X = CN
2d: X = NO_2

Table S2-1. Maximum absorption wavelengths of [*c*2]daisy chain rotaxane **2a**–**d**.

	2a (X = H)$^{a)}$	**2b** (X = OMe)	**2c** (X = CN)	**2d** (X = NO_2)
	λ_{abs} (nm)	λ_{abs} (nm)	λ_{abs} (nm)	λ_{abs} (nm)
$CHCl_3$	297, 316	296	299	299
THF	296, 315	294	297	298
MeOH	296, 315	294	297	297
MeCN	296, 315	294	297	297
DMSO	297, 316	295	298	298

[**2**] = 1.3×10^{-5}–1.7×10^{-5} M. $^{a)}$previous reported.[s2]



R = $(CH_2CH_2O)_3H$

3a: X = H
3b: X = OMe
3c: X = CN
3d: X = NO_2

Table S2-2. Maximum absorption wavelengths of stoppered monomer **3a**–**d**.

	3a (X = H)$^{a)}$	**3b** (X = OMe)	**3c** (X = CN)	**3d** (X = NO_2)
	λ_{abs} (nm)	λ_{abs} (nm)	λ_{abs} (nm)	λ_{abs} (nm)
$CHCl_3$	296, 315	299, 319	297	297, 314
THF	295, 314	296, 318	296	296, 314
MeOH	293, 311	292, 315	294	294, 311
MeCN	294, 313	295, 317	294	294, 312
DMSO	297, 316	302, 321	298	298, 315

[**3**] = 3.2×10^{-5}–4.0×10^{-5} M. $^{a)}$previous reported.[s2]

5. Maximum emission wavelengths in fluorescence spectra (Table S3)

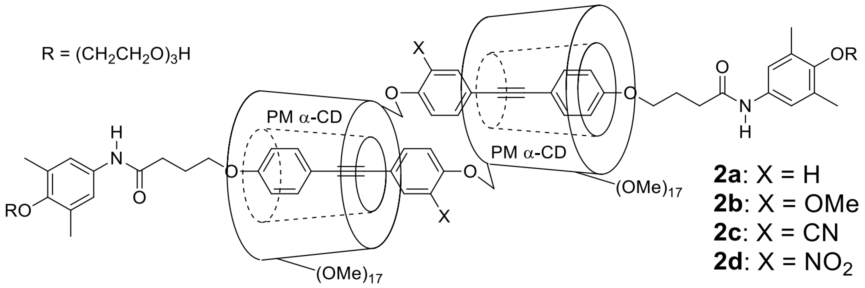


Table S3-1. Maximum emission wavelengths of [*c*2]daisy chain rotaxane **2a**–**d**.

	2a (X = H)[a)]	**2b** (X = OMe)	**2c** (X = CN)	**2d** (X = NO_2)
	λ_{flu} (nm)	λ_{flu} (nm)	λ_{flu} (nm)	λ_{flu} (nm)
$CHCl_3$	323, 335, 355	329, 343	370	327, 366
THF	322, 337, 357	326, 342	370	---
MeOH	322, 336, 358	328, 344	380	---
MeCN	322, 335, 360	328, 341	377	---
DMSO	323, 337, 361	328, 344	376	---

[**2**] = 2.6×10^{-7}–8.0×10^{-7} M. [a)]previous reported.[s2]

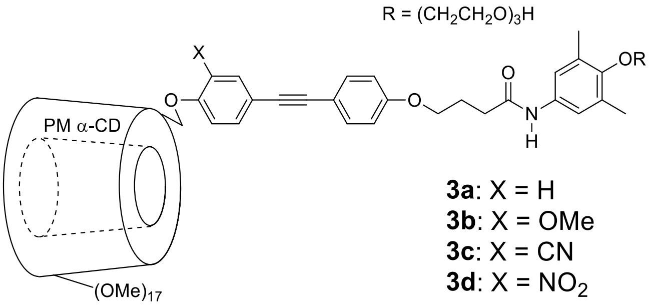


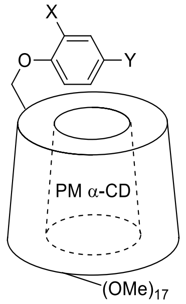
Table S3-2. Maximum emission wavelengths of stoppered monomer **3a**–**d**.

	3a (X = H)[a)]	**3b** (X = OMe)	**3c** (X = CN)	**3d** (X = NO_2)
	λ_{flu} (nm)	λ_{flu} (nm)	λ_{flu} (nm)	λ_{flu} (nm)
$CHCl_3$	323, 336, 344	329, 342	375	328, 363
THF	322, 334, 344	327, 342	372	---
MeOH	319, 333, 340	325, 339	390	---
MeCN	322, 333, 343	326, 341	387	---
DMSO	326, 338, 347	333, 346	388	---

[**3**] = 1.5×10^{-6}–2.0×10^{-6} M. [a)]previous reported.[s2]

6. Synthetic procedures, and ^{1}H and ^{13}C NMR spectra (Figure 1–19)

6-1. PM α-CD halide **S1**



S1a: X = H, Y = I
S1b: X = OMe, Y = Br
S1c: X = CN, Y = Br
S1d: X = NO$_2$, Y = Br

General procedure

4-Bromo-2-cyanophenol (0.69 g, 3.5 mmol) and PM α-CD-OTs (4.0 g, 2.9 mmol) were dissolved in dry DMF (40 mL). Anhydrous K_2CO_3 (1.0 g, 7.2 mmol) was added to the solution and the mixture was stirred under nitrogen at 100 °C for 13 h and cooled to room temperature. The mixture was diluted with EtOAc and washed with saturated $NaHCO_3$aq. and brine. The organic layer was separated and dried over Na_2SO_4. The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel (EtOAc/toluene (1/1) and then EtOAc/MeOH (9/1)) to yield PM α-CD iodide **S1c** as a white formed solid (3.7 g, 92%).

S1a: 97%; This compound was previously reported.[s2] ^{1}H NMR spectrum was shown in Figure S1.
S1b: 93%; m.p.: 223-225 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 22.4 °C): δ_H = 6.99-6.97 (m, 2H), 6.81 (d, J = 8.9 Hz, 1H), 5.11-5.00 (m, 6H), 4.39 (d, J = 10.4 Hz, 1H), 4.30 (dd, J = 5.1, 10.5 Hz, 1H), 4.06 (dd, J = 5.0, 9.4 Hz, 1H), 3.98 (dd, J = 3.4, 10.8 Hz, 1H), 3.85-3.11 (m, 86H); ^{13}C NMR (100 MHz, $CDCl_3$, 22.4 °C): δ_C = 150.05, 147.38, 122.70, 115.01, 114.74, 112.96, 99.69-99.61 (several peaks overlapped), 82.48, 81.98-81.60 (several peaks overlapped), 80.71, 77.19, 70.99-70.68 (several peaks overlapped), 70.28, 68.84, 61.34-61.25 (several peaks overlapped), 58.46-58.41 (several peaks overlapped), 58.30, 57.30-57.26 (several peaks overlapped), 55.41; ESI-TOF-HRMS: (*m/z*) 1417.5269 ([M·Na]$^{+}$, $C_{60}H_{99}BrO_{31}Na$, Calcd. 1417.5246)
S1c: 92%; m.p.: 233-235 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 21.8 °C): δ_H = 7.68 (d, J = 2.5 Hz, 1H), 7.63 (dd, J = 2.5, 9.0 Hz, 1H), 6.95 (d, J = 9.0 Hz, 1H), 5.09-4.97 (m, 6H), 4.49 (d, J = 9.9 Hz, 1H), 4.43 (dd, J = 5.2, 10.3 Hz, 1H), 4.21 (dd, J = 4.8, 9.8 Hz, 1H), 4.02 (dd, J = 3.0, 11.0 Hz, 1H), 3.92-3.11 (m, 83H); ^{13}C NMR (100 MHz, $CDCl_3$, 21.7 °C): δ_C = 159.48, 136.86, 135.52, 114.55, 114.30, 112.55, 103.87, 100.08, 99.98-99.95 (several peaks overlapped), 99.57, 82.65, 82.38, 82.20, 82.13-82.05 (several peaks overlapped), 81.90-81.85 (several peaks overlapped), 81.70, 81.11-81.06 (several peaks overlapped), 80.83, 77.20, 71.07-70.83 (several peaks overlapped), 70.10, 61.79, 61.73, 61.70,

61.62-61.58 (several peaks overlapped), 58.89-58.85 (several peaks overlapped), 58.79, 58.54, 57.77, 57.70, 57.64-57.58 (several peaks overlapped); ESI-TOF-HRMS: (*m/z*) 1412.5099 ($[M\cdot Na]^+$, $C_{60}H_{96}BrNO_{30}Na$, Calcd. 1412.5093)

S1d: 90%; m.p.: 223-225 °C; ^1H NMR (400 MHz, $CDCl_3$, 22.0 °C): δ_H = 7.95 (d, *J* = 2.5 Hz, 1H), 7.63 (dd, *J* = 2.5, 8.9 Hz, 1H), 7.06 (d, *J* = 8.9 Hz, 1H), 5.10-4.97 (m, 6H), 4.52 (dd, *J* = 5.2, 10.2 Hz, 1H), 4.44 (d, *J* = 9.7 Hz, 1H), 4.15 (m, 1H), 3.95-3.10 (m, 84H); ^{13}C NMR (100 MHz, $CDCl_3$, 22.1 °C): δ_C = 151.06, 140.39, 136.39, 127.86, 116.65, 112.04, 100.06-99.98 (several peaks overlapped), 99.80, 99.52, 82.52, 82.38, 82.21, 82.12-82.04 (several peaks overlapped), 81.92-81.85 (several peaks overlapped), 81.75, 81.08-81.03 (several peaks overlapped), 80.83, 77.20, 71.16-70.95 (several peaks overlapped), 70.67, 70.34, 61.80, 61.73, 61.71, 61.66-61.62 (several peaks overlapped), 58.92-58.89 (several peaks overlapped), 58.81, 58.58, 57.75, 57.69-57.67 (several peaks overlapped), 57.63; ESI-TOF-HRMS: (*m/z*) 1432.5057 ($[M\cdot Na]^+$, $C_{59}H_{96}BrNO_{32}Na$, Calcd. 1432.4991)

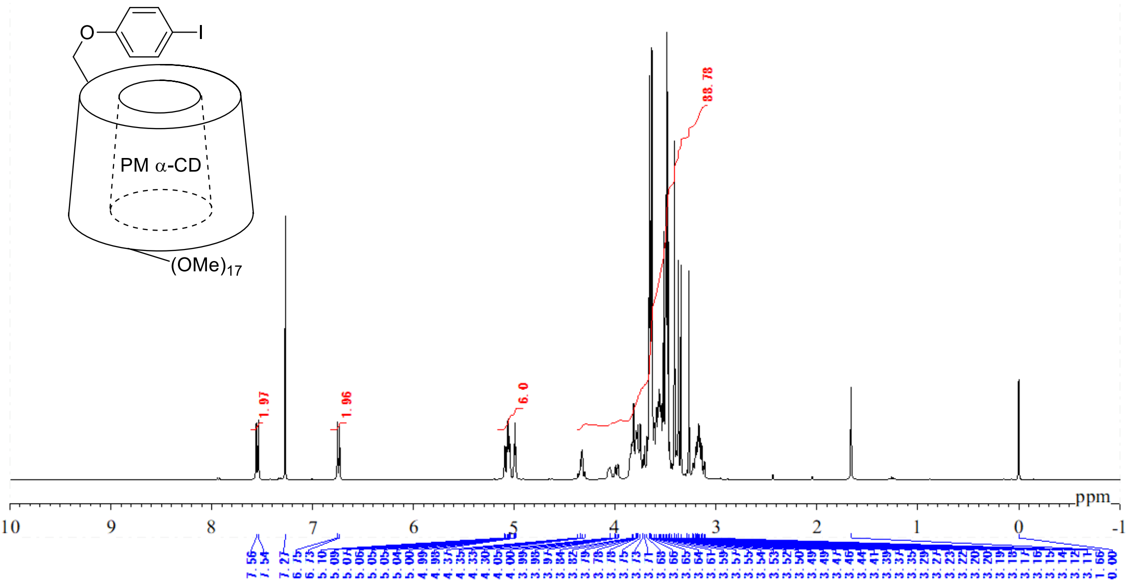


Figure S1. ^{1}H NMR spectrum of PM α-CD Iodide **S1a**.

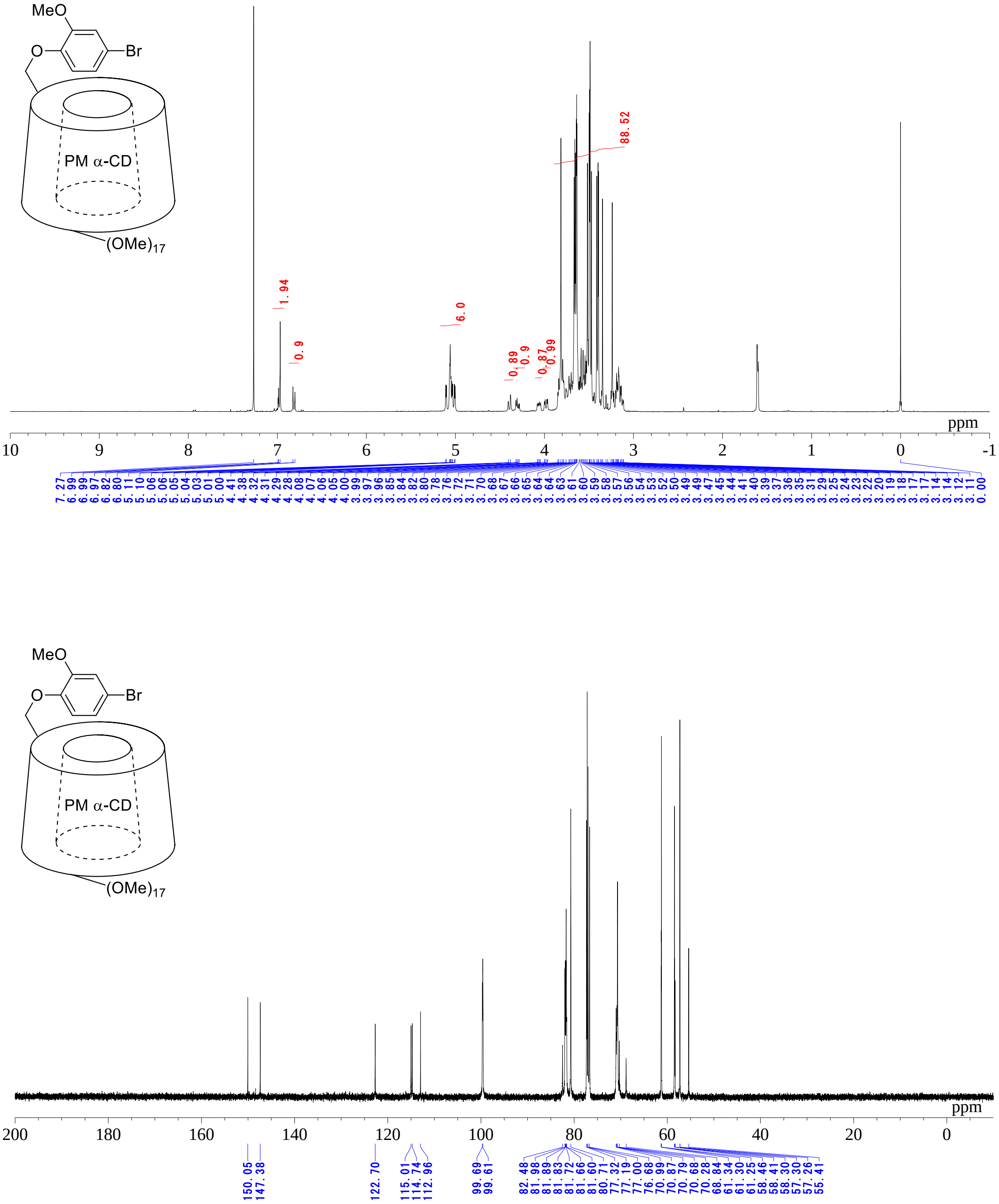


Figure S2. ^{1}H and ^{13}C NMR spectra of PM α-CD bromide **S1b**.

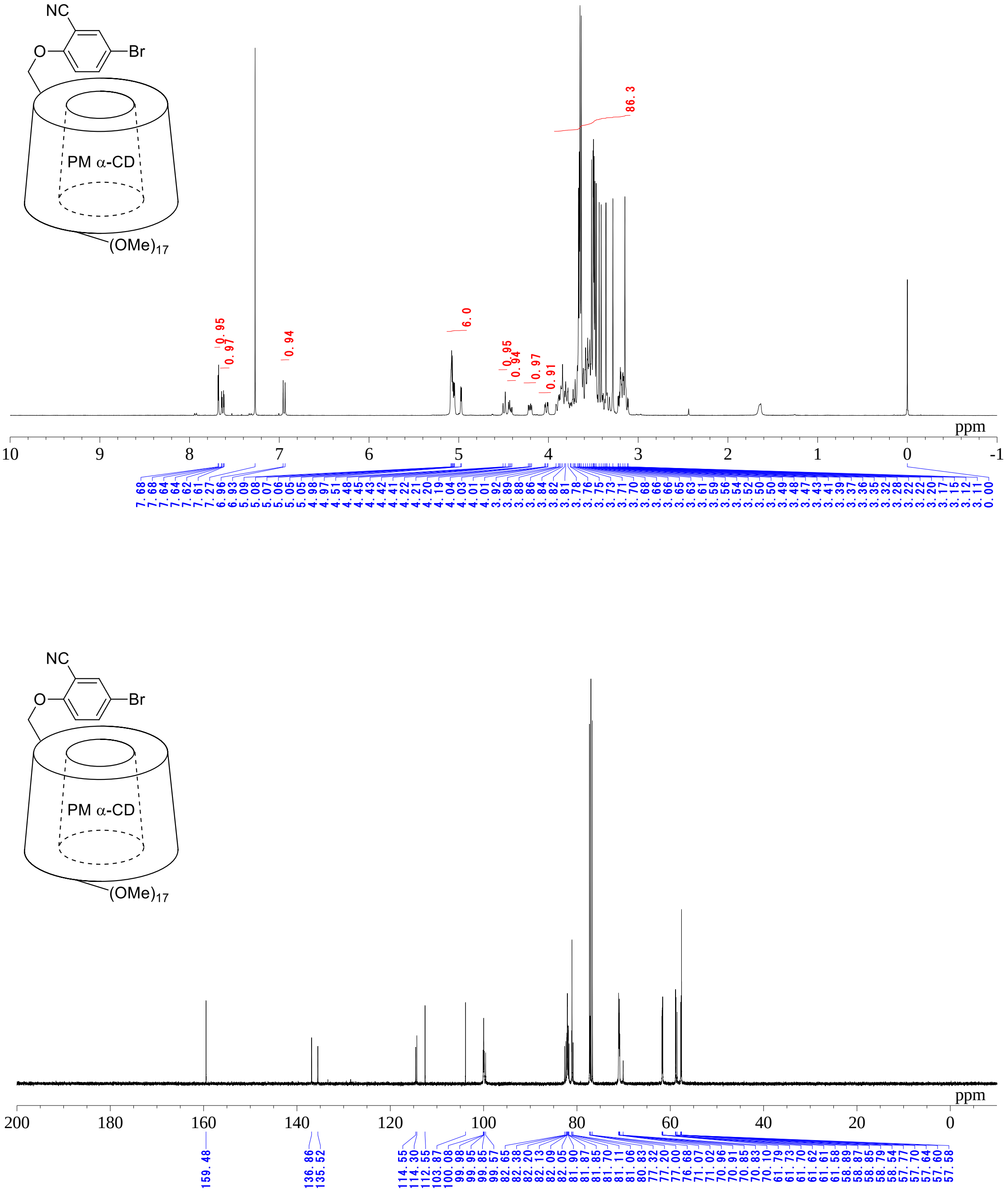


Figure S3. ^{1}H and ^{13}C NMR spectra of PM α-CD bromide **S1c**.

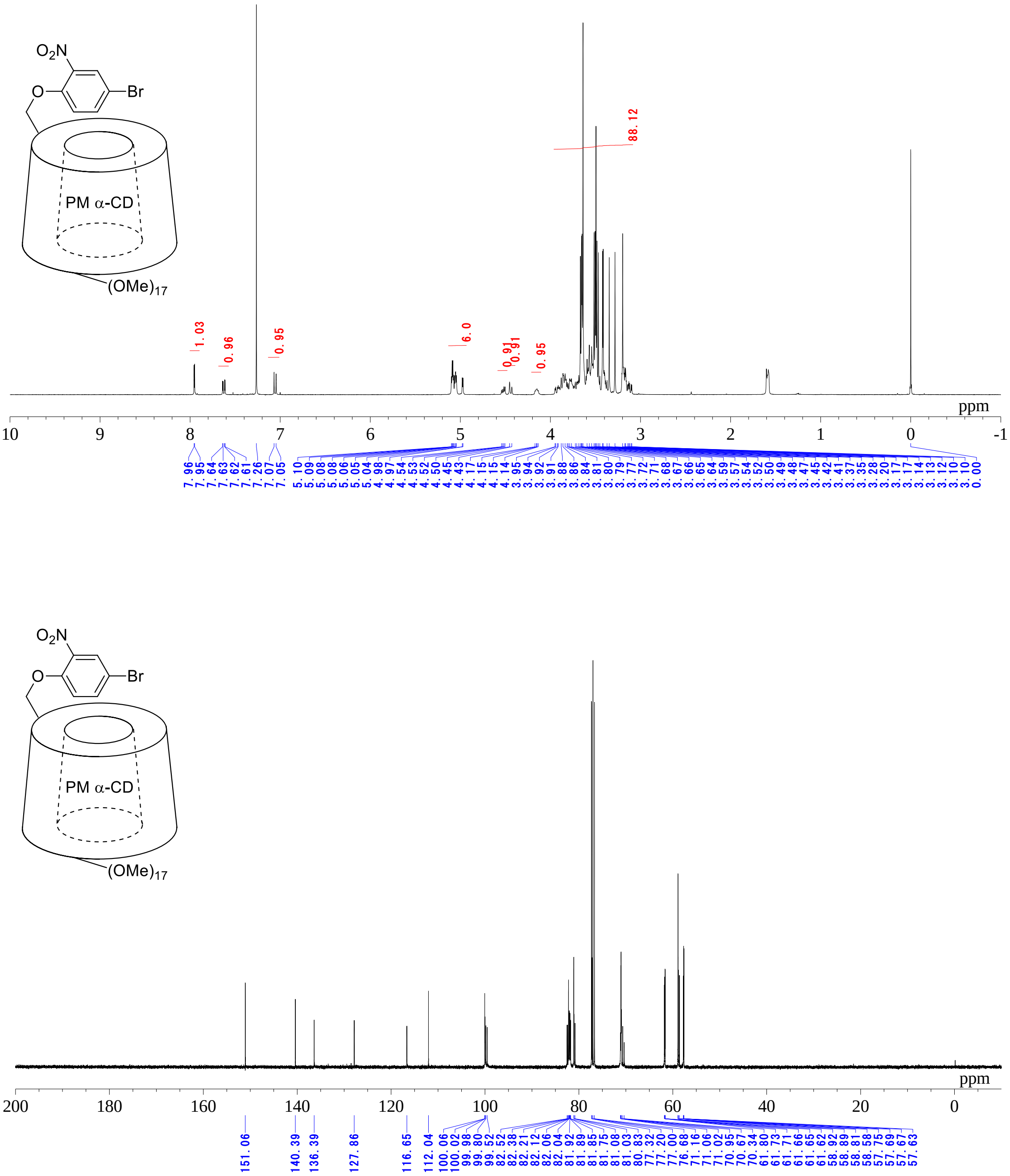
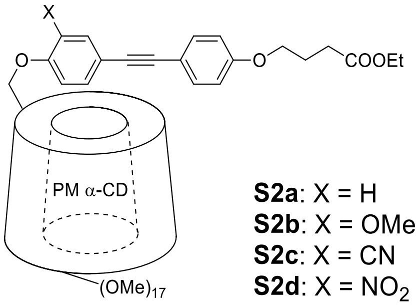


Figure S4. ^{1}H and ^{13}C NMR spectra of PM α-CD bromide **S1d**.

6-2. PM α-CD ethyl ester **S2**



S2a: X = H
S2b: X = OMe
S2c: X = CN
S2d: X = NO_2

General Procedure

PM α-CD bromide **S1c** (1.0 g, 0.72 mmol), ethyl 4-(4-ethynylphenoxy)butyrate (0.86 g, 3.7 mmol), $Pd(PPh_3)_4$ (81 mg, 0.070 mmol), and CuI (6.6 mg, 0.035 mmol) were dissolved in *i*-Pr_2NH/THF (2/1) (30 mL) degassed with N_2 bubbling for 20 min. Under N_2 atmosphere, the mixture was stirred for 24 h. The mixture was diluted with EtOAc and washed with saturated NH_4Claq. and brine. The organic layer was separated and dried over Na_2SO_4. The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel (EtOAc/$CHCl_3$ (1/1) and then EtOAc/MeOH (95/5)) to yield PM α-CD ethyl ester **S2c** as a pale brown solid (1.0 g, 90%).

S2a: 89%; This compound was previously reported. [s2] ^{1}H NMR spectrum was shown in Figure S5.
S2b: the crude containing **S2b** was used to next reaction without purification.
S2c: 90%; m.p.: 112-115 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 22.5 °C): δ_H = 7.71 (d, *J* = 2.1 Hz, 1H), 7.65 (dd, *J* = 2.1, 8.8 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 1H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.10-4.97 (m, 6H), 4.56 (d, *J* = 10.0 Hz, 1H), 4.42 (dd, *J* = 5.4, 10.1 Hz, 1H), 4.24 (dd, *J* = 5.2, 9.8 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 4.09-4.01 (m, 3H), 3.94-3.12 (m, 83H), 2.52 (t, *J* = 7.3 Hz, 2H), 2.12 (m, 2H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 22.5 °C): δ_C = 172.90, 159.55, 159.05, 136.87, 136.09, 132.85, 117.06, 114.93, 114.45, 114.35, 112.96, 102.42, 100.11, 100.01, 99.95, 99.81, 99.52, 90.01, 85.17, 82.79, 82.34, 82.16-81.88 (several peaks overlapped), 81.72, 81.16-81.10 (several peaks overlapped), 80.88, 77.20, 71.10-70.90 (several peaks overlapped), 70.82, 70.13, 66.63, 61.81, 61.74, 61.70, 61.63-61.58 (several peaks overlapped), 60.29, 58.91, 58.87, 58.83, 58.78, 58.60, 57.82, 57.68, 57.62, 57.59, 30.50, 24.32, 14.05; ESI-TOF-HRMS: (*m/z*) 1564.6937 ($[M{\cdot}Na]^+$, $C_{74}H_{111}NO_{33}Na$, Calcd. 1564.6931)

S2d: 96%; m.p.: 116-117 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 20.2 °C): δ_H = 7.95 (d, *J* = 2.1 Hz, 1H), 7.64 (dd, J = 2.1, 8.7 Hz, 1H), 7.42 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.7 Hz, 1H), 6.86 (d, J = 8.3 Hz, 1H), 5.12-4.98 (m, 6H), 4.54-4.48 (m, 2H), 4.20-4.12 (m, 3H), 4.03 (t, J = 6.1 Hz, 2H), 3.98 (dd, J = 3.0, 10.9 Hz, 1H), 3.92-3.11 (m, 83H), 2.52 (t, J = 7.3 Hz, 2H), 2.12 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, 20.2 °C): δ_C = 173.01, 159.18, 151.27, 139.84, 136.36, 132.97, 127.95, 116.58, 115.01, 114.53, 114.32, 100.12-99.91 (several peaks overlapped), 99.48, 90.33, 85.15, 82.57, 82.53, 82.25-81.94 (several peaks overlapped), 81.82, 81.22-81.11 (several peaks overlapped), 80.91, 77.20, 71.11-70.98 (several peaks overlapped), 70.82, 70.40, 66.71, 61.88, 61.80-61.69 (several peaks overlapped), 60.39, 58.95, 58.83, 58.70, 57.81, 57.78, 57.72-57.67 (several peaks overlapped), 30.58, 24.39, 14.13; ESI-TOF-HRMS: (*m/z*) 1584.6818 ($[M{\cdot}Na]^+$, $C_{73}H_{111}NO_{35}Na$, Calcd. 1584.6829)

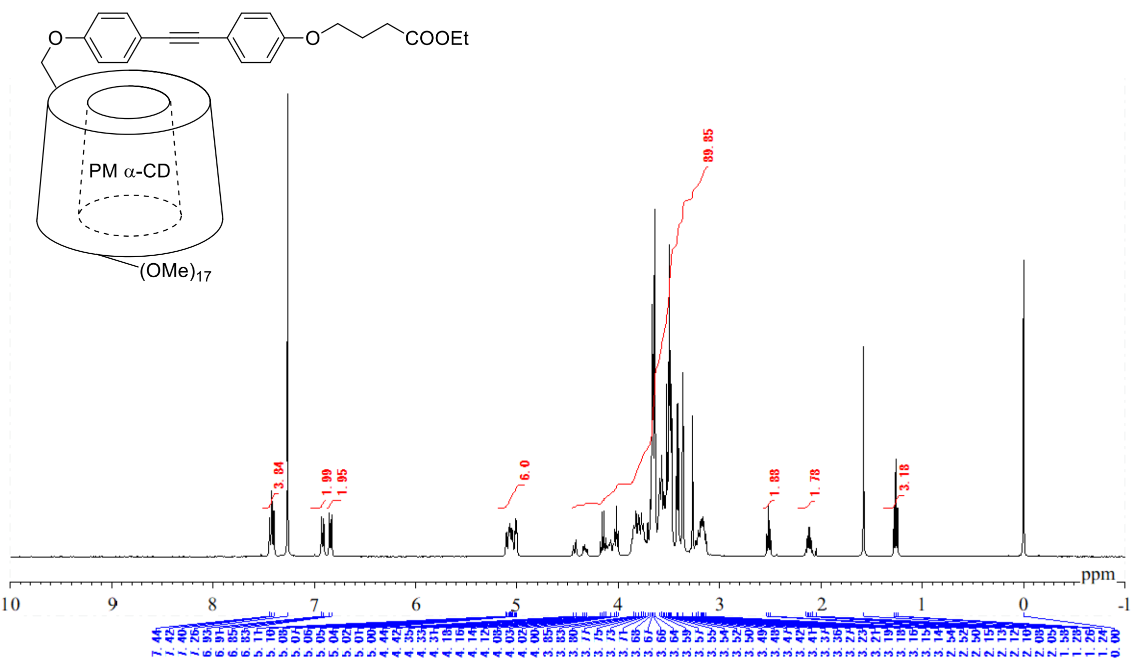


Figure S5. ^{1}H NMR spectrum of PM α-CD ethyl ester **S2a**.

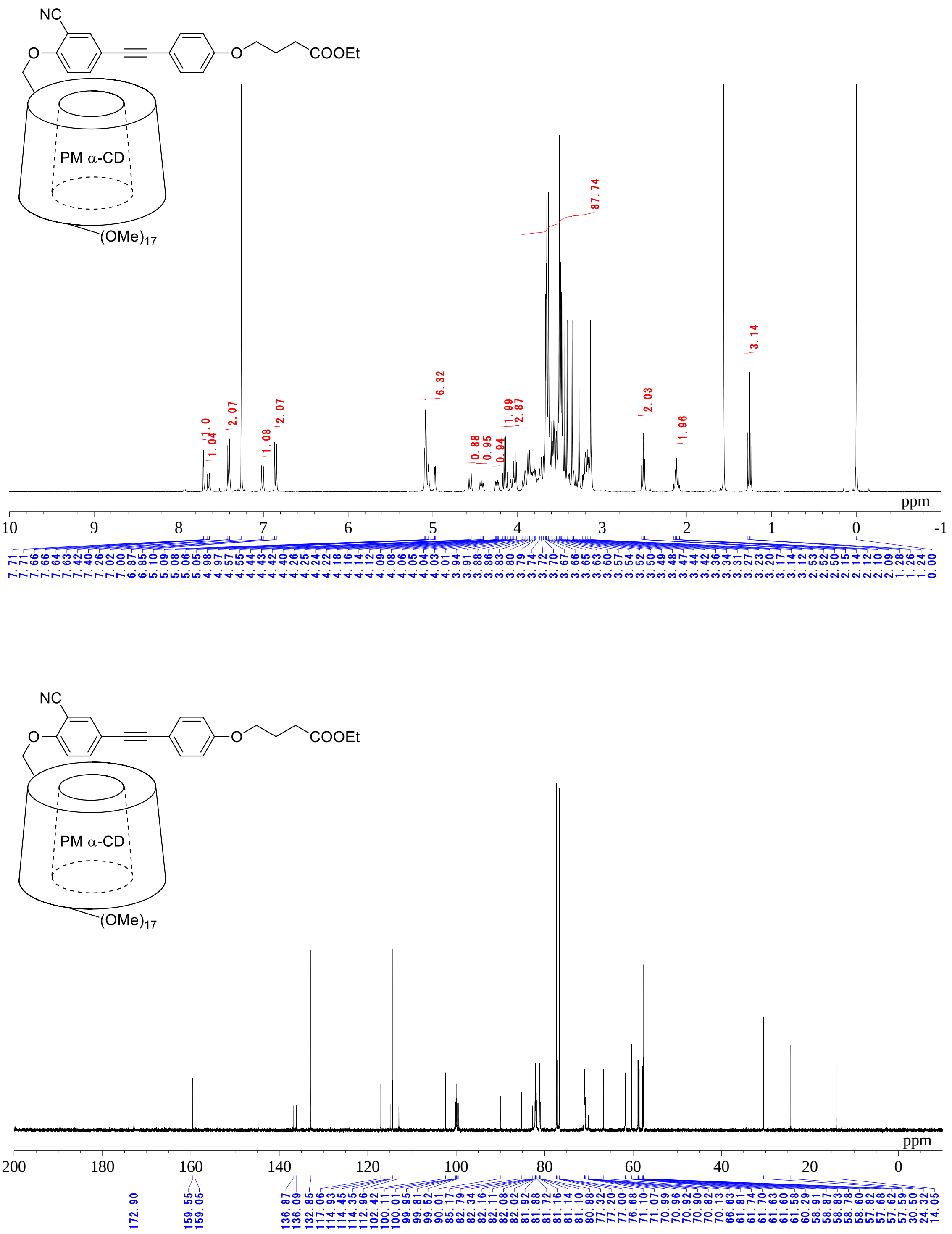


Figure S6. ^{1}H and ^{13}C NMR spectra of PM α-CD ethyl ester **S2c**.

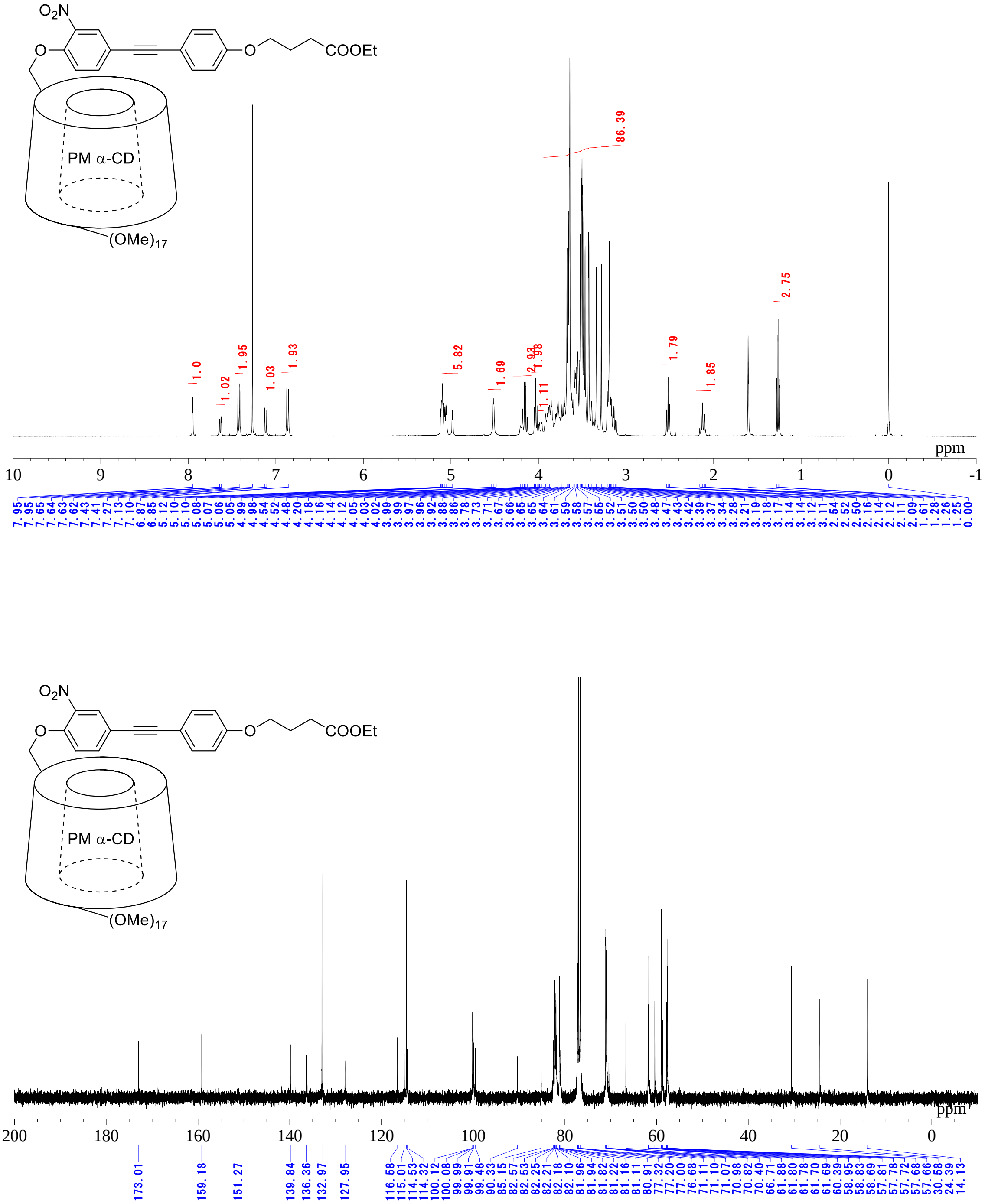
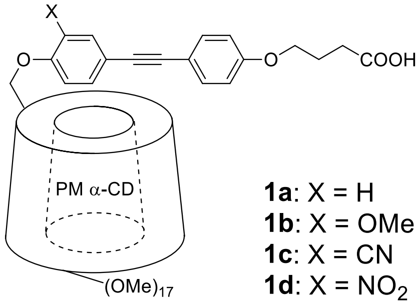


Figure S7. ^{1}H and ^{13}C NMR spectra of PM α-CD ethyl ester **S2d**.

6-3. Monomer **1**



1a: X = H
1b: X = OMe
1c: X = CN
1d: X = NO_2

General Procedure

PM α-CD ethyl ester **S2c** (0.91 g, 0.59 mmol) was dissolved in mixture solvent of MeOH (30 mL) and 1 mol/L aqueous KOH (6.0 mL). The resulting mixture was stirred for 1 h at 60 °C under N_2 atmosphere. The mixture was cooled to room temperature, diluted with Chloroform and washed with 2 mol/L aqueous HCl and brine. The organic layer was separated and dried over $MgSO_4$. The solvent was removed *in vacuo* to yield monomer **1c** as a pale yellow formed solid (0.89 g, quant.).

1a: 89%; This compound was previously reported.[s2] ^1H NMR spectrum was shown in Figure S8.

1b: After ester hydrolysis, the crude was purified by column chromatography on silica gel (EtOAc/MeOH (95/5)) to obtain monomer **1b** in 35% yield in 2 steps from PM α-CD bromide **S1b**; m.p.: 121-123 °C; ^1H NMR (400 MHz, $CDCl_3$, 22.4 °C): δ_H = 7.42 (d, *J* = 8.9 Hz, 2H), 7.05 (dd, *J* = 1.8, 8.3 Hz, 1H), 7.01 (d, *J* = 1.8 Hz, 1H), 6.89 (d, *J* = 8.3Hz, 1H), 6.84 (d, *J* = 8.9 Hz, 2H), 5.11-5.00 (m, 6H), 4.49 (d, *J* = 9.7 Hz, 1H), 4.31 (dd, *J* = 5.6, 10.5 Hz, 1H), 4.11-4.02 (m, 4H), 3.85-3.12 (m, H), 2.58 (t, *J* = 7.2 Hz, 2H), 2.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 20.6 °C): δ_C = 176.22, 158.47, 148.98, 148.49, 132.63, 124.17, 116.21, 115.26, 114.40, 114.24, 113.45, 99.95, 99.85-99.77 (several peaks overlapped), 87.79, 82.89, 82.11-81.76 (several peaks overlapped), 81.00, 77.20, 71.18-70.79 (several peaks overlapped), 70.55, 68.87, 66.40, 61.62-61.52 (several peaks overlapped), 58.75-58.67 (several peaks overlapped), 57.59-57.55 (several peaks overlapped), 55.47, 30.03, 24.15; ESI-TOF-HRMS: (*m/z*) 782.3329 ($[M{\cdot}2Na]^{2+}$, $C_{72}H_{110}O_{34}Na_2$, Calcd. 782.3332)

1c: quant.; m.p.: 142-145 °C; ^1H NMR (400 MHz, $CDCl_3$, 19.3 °C): δ_H = 7.71 (d, *J* = 2.1 Hz, 1H), 7.65 (dd, *J* = 2.1, 8.8 Hz, 1H), 7.41 (d, *J* = 8.9 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 1H), 6.86 (d, *J* = 8.9 Hz, 2H), 5.10-4.97 (m, 6H), 4.56 (d, *J* = 9.9 Hz, 1H), 4.42 (dd, *J* = 5.5, 10.4 Hz, 1H), 4.25 (dd, *J* = 5.2, 9.9 Hz, 1H), 4.09-4.03 (m, 3H), 3.94-3.12 (m, 84H), 2.58 (t, *J* = 7.3 Hz, 2H), 2.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 20.1 °C): δ_C = 176.54, 159.52, 158.98, 136.89, 136.07, 132.84, 117.03, 114.94, 114.41, 114.37, 112.94, 102.36, 100.05, 99.94-99.89 (several peaks overlapped), 99.75, 99.47, 89.99, 85.17, 82.69, 82.27, 82.08-81.78 (several peaks overlapped), 81.63, 81.17-81.10 (several peaks overlapped), 80.88, 77.20, 71.07-70.78 (several peaks overlapped), 70.10-70.05 (several peaks overlapped), 66.49, 61.78, 61.72, 61.68, 61.60-61.55 (several peaks overlapped), 58.89, 58.86, 58.81, 58.76, 58.58, 57.82, 57.67, 57.61-57.57 (several peaks overlapped), 30.07, 24.15; ESI-TOF-HRMS: (*m/z*) 779.8272 ($[M{\cdot}2Na]^{2+}$, $C_{72}H_{107}NO_{33}Na_2$, Calcd. 779.8255)

1d: 99%; m.p.: 149-152 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 20.1 °C): δ_H = 7.95 (d, *J* = 2.1 Hz, 1H), 7.64 (dd, *J* = 2.1, 8.7 Hz, 1H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.12-5.05 (m, 6H), 4.52 (m, 2H), 4.19 (m, 1H), 4.04 (t, *J* = 6.1 Hz, 2H), 3.99-3.11 (m, 85H), 2.58 (t, *J* = 7.3 Hz, 2H), 2.13 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 20.0 °C): δ_C = 177.27, 159.14, 151.31, 139.85, 136.41, 133.03, 128.00, 116.59, 115.03, 114.55, 114.45, 100.15-100.10 (several peaks overlapped), 100.01, 99.93, 99.52, 90.33, 85.23, 82.55, 82.26-82.17 (several peaks overlapped), 82.11, 81.96-81.94 (several peaks overlapped), 81.82, 81.28-81.16 (several peaks overlapped), 80.97, 77.20, 71.15-71.11 (several peaks overlapped), 71.02, 70.85, 70.40, 66.57, 61.92, 61.84-61.82 (several peaks overlapped), 61.74-61.72 (several peaks overlapped), 59.00-58.99 (several peaks overlapped), 58.87, 58.73, 57.85, 57.83, 57.76, 57.73, 57.71, 30.17, 24.23; ESI-TOF-HRMS: (*m/z*) 789.8195 ($[M{\cdot}2Na]^{2+}$, $C_{71}H_{107}NO_{35}Na_2$, Calcd.789.8204)

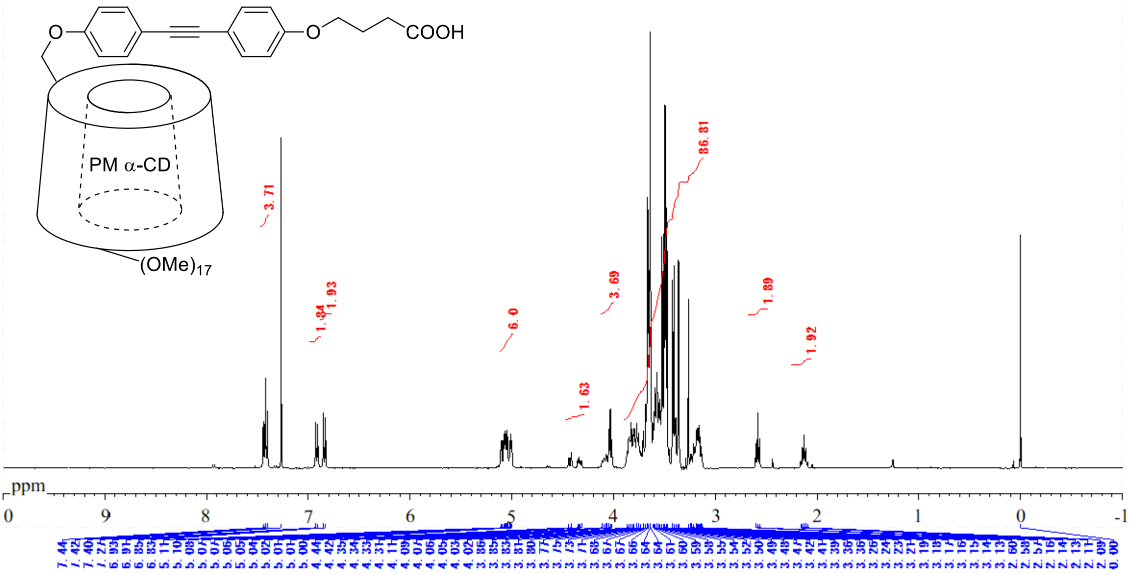


Figure S8. ^{1}H NMR spectrum of monomer **1a**.

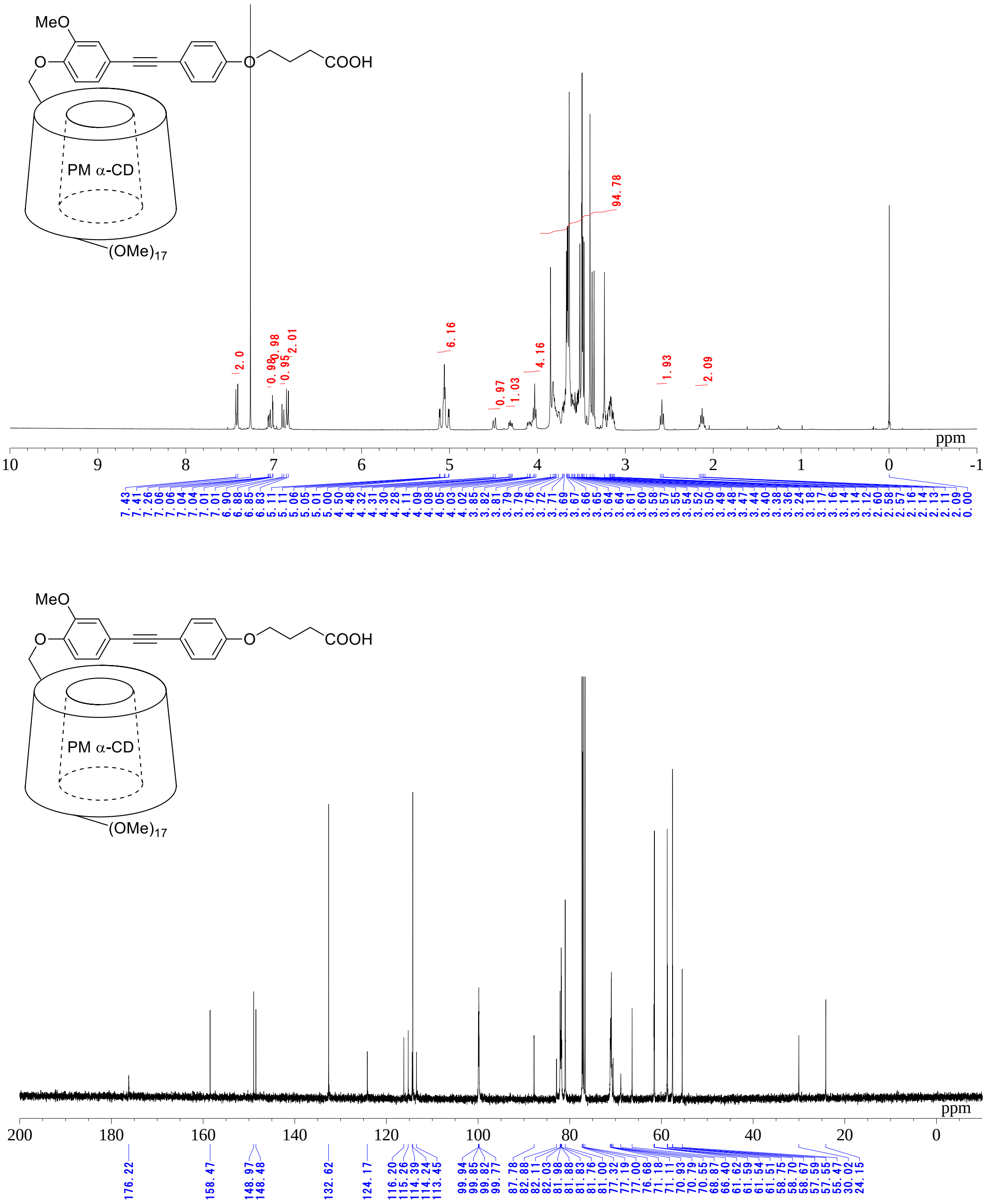


Figure S9. ^{1}H and ^{13}C NMR spectra of monomer **1b**.

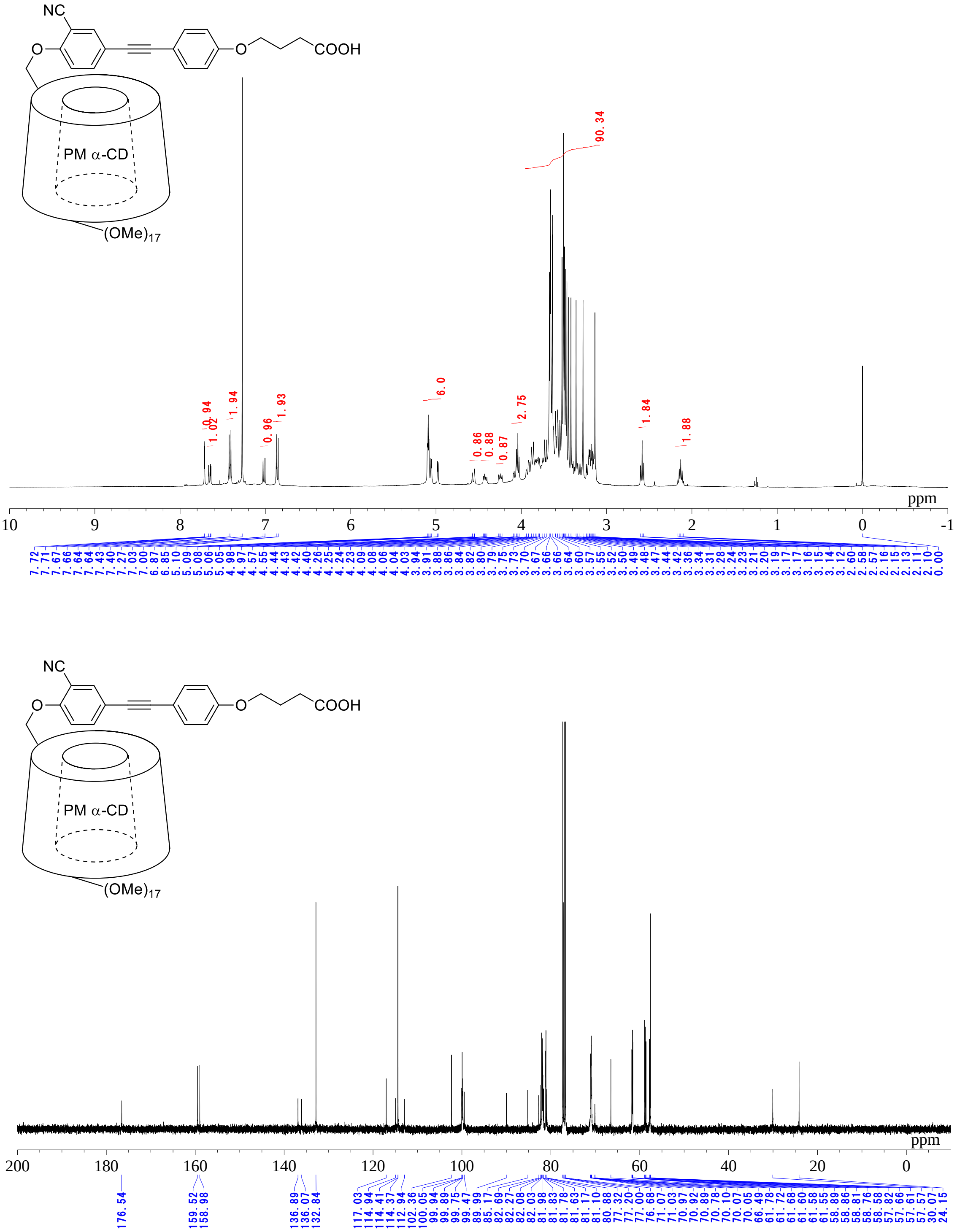


Figure S10. ^{1}H and ^{13}C NMR spectra of monomer **1c**.

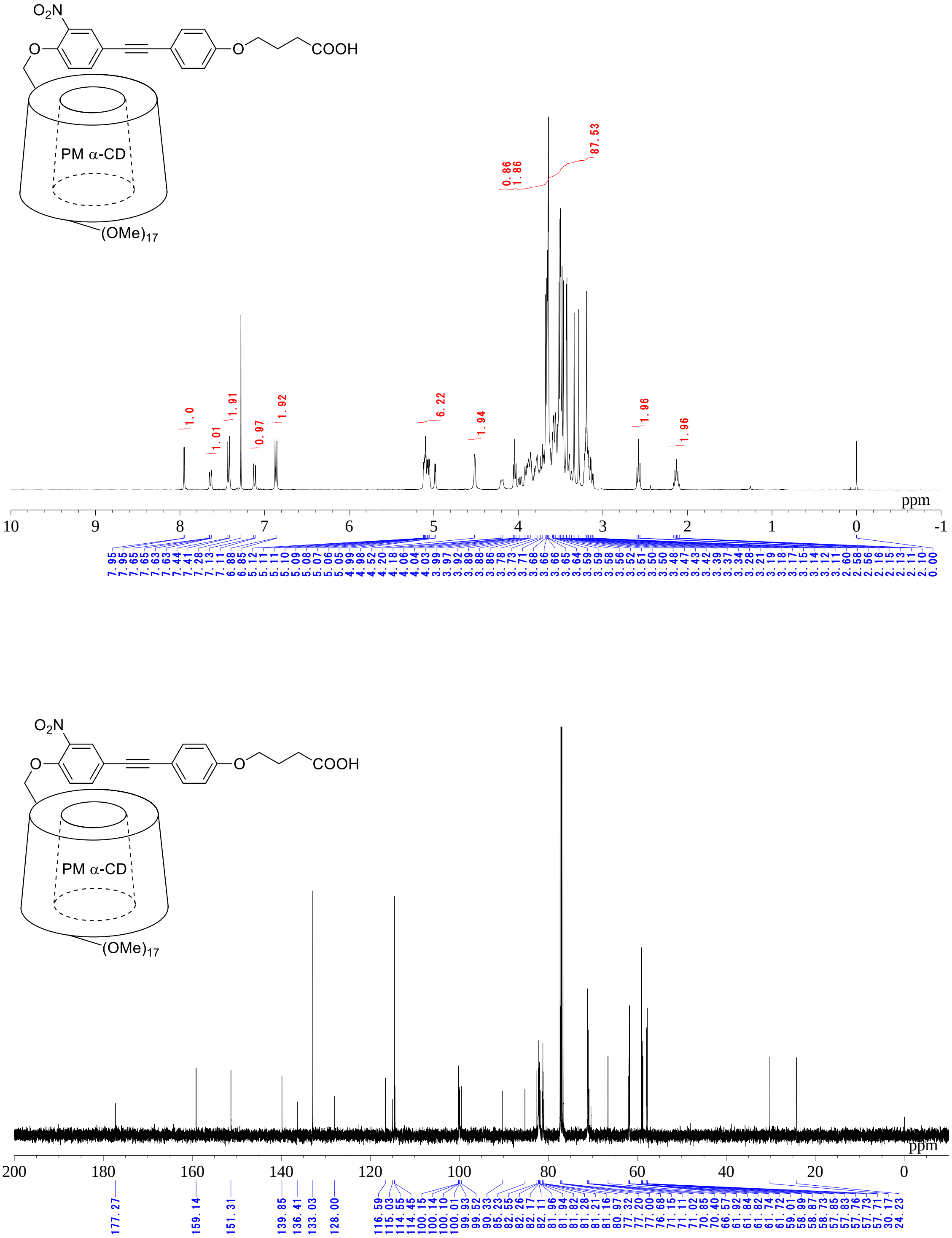
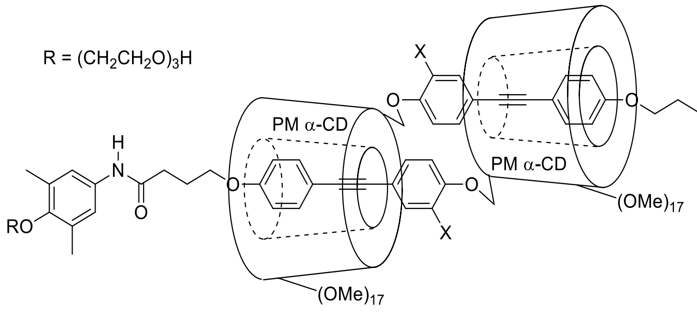


Figure S11. ^{1}H and ^{13}C NMR spectra of monomer **1d**.

6-4. [*c*2]Daisy chain rotxane **2**



2a: X = H
2b: X = OMe
2c: X = CN
2d: X = NO_2

General Procedure

Monomer **1c** (107 mg, 0.070 mmol) and 4-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}-3,5-dimethylaniline (113 mg, 0.42 mmol) were dissolved in MeOH/H_2O (1/2) (10 mL). After cooling the solution at below 2 °C, 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl) (79.2 mg, 0.41 mmol) was added to the solution. The reaction mixture was stirred at below 2 °C for 2 h, and then stirred at room temperature for an additional 4 h. The reaction mixture was acidified with dilute HClaq., diluted with EtOAc and washed with brine. The organic layer was separated and dried over $MgSO_4$. The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel (EtOAc/MeOH (4/1)) to yield [*c*2]daisy chain rotaxane **2c** as a white formed solid (75.8 mg, 61%).

2a: 49%; This compound was previously reported.[s2] ^{1}H NMR spectrum was shown in Figure S12.

2b: 68%; m.p.: decomposition > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 21.1 °C): δ_H = 7.98 (d, *J* = 8.6 Hz, 4H), 7.14 (s, 4H), 7.05-6.98 (m, 8H), 6.84 (d, *J* = 1.7 Hz, 2H), 6.59 (d, *J* = 8.4 Hz 2H), 5.13-4.99 (m, 12H), 4.32-2.89 (m, 208H), 2.45 (t, *J* = 7.4 Hz, 4H), 2.34 (t, *J* = 6.2 Hz, 2H), 2.27 (s, 12H), 2.17 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 21.6 °C): δ_C = 169.76, 159.35, 152.25, 150.50, 150.21, 134.41, 133.23, 131.44, 126.09, 120.24, 117.78, 116.25, 115.71, 114.14, 113.95, 100.50, 100.27-100.17 (several peaks overlapped), 99.82, 99.49, 88.69, 87.77, 82.52, 82.16-81.71 (several peaks overlapped), 81.46, 81.02, 80.84, 80.69-80.64 (several peaks overlapped), 77.20, 72.62, 72.41, 71.87, 71.59, 71.48-71.34 (several peaks overlapped), 71.15-70.94 (several peaks overlapped), 70.80, 70.57, 70.46, 70.41, 69.93, 66.71, 61.79, 61.70-61.69 (several peaks overlapped), 61.59, 61.50, 59.50, 59.14-59.12 (several peaks overlapped), 59.03, 58.86, 57.89-57.87 (several peaks overlapped), 57.78-57.74 (several peaks overlapped), 57.62, 33.41, 24.85, 16.29; ESI-TOF-HRMS: (*m/z*) 1202.8820 ($[M\cdot 3Na]^{3+}$, $C_{172}H_{262}N_2O_{74}Na_3$, Calcd. 1202.8826).

2c:61%; m.p.: decomposition > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 20.9 °C): δ_H = 8.01 (d, *J* = 8.5 Hz, 4H), 7.64-7.62 (m, 4H), 7.14 (s, 4H), 7.05-7.02 (m, 6H), 6.76 (d, *J* = 8.7 Hz, 2H), 5.12-4.95 (m, 12H), 4.40-4.29 (m, 4H), 4.18-3.04 (m, 194H), 2.93-2.86 (m, 4H), 2.45 (t, *J* = 7.3 Hz, 4H), 2.35 (t, *J* = 6.1 Hz, 2H), 2.27 (s, 12H), 2.17 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 21.8 °C): δ_C = 169.71, 160.18, 159.77, 152.18, 136.79, 134.51, 133.22, 131.37, 120.24-120.13 (several peaks overlapped), 116.94, 114.47, 114.11-114.02 (several peaks overlapped), 113.28, 103.52, 100.52-99.99 (several peaks overlapped), 99.85, 99.37, 99.23, 91.06, 85.39, 82.71, 82.56, 82.44, 82.31, 82.17-81.89 (several peaks overlapped), 81.69, 81.54, 81.26-81.22 (several peaks overlapped), 81.07, 80.67-80.47 (several peaks overlapped), 77.12, 72.64, 72.40, 71.94-71.86 (several peaks overlapped), 71.58-71.38 (several peaks overlapped), 71.16-71.10 (several peaks overlapped), 70.73-70.60 (several peaks overlapped), 70.40-70.32 (several peaks overlapped), 70.06, 66.76, 61.66-61.38 (several peaks overlapped), 59.46, 59.26, 59.07-58.98 (several peaks overlapped), 57.89-57.87 (several peaks overlapped), 57.76, 57.61, 57.55, 33.25, 24.74, 16.25; ESI-TOF-HRMS: (*m/z*) 1199.5365 ($[M\cdot 3Na]^{3+}$, $C_{172}H_{256}N_4O_{72}Na_3$, Calcd. 1199.5390).

2d: 10%; m.p.: decomposition > 300 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 21.3 °C): $\delta_H = 8.01$ (d, $J = 8.7$ Hz, 4H), 7.75 (d, $J = 1.9$ Hz, 2H), 7.68 (dd, $J = 1.9$, 8.6 Hz, 2H), 7.14 (s, 4H), 7.07-7.03 (m, 6H), 6.96 (d, $J = 8.6$ Hz, 2H), 5.15-4.96 (m, 12H), 4.49 (m, 2H), 4.25 (m, 2H), 4.17-3.03 (m, 194H), 2.89-2.83 (m, 4H), 2.45 (t, $J = 7.2$ Hz, 4H), 2.30-2.27 (m, 14H), 2.17 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$, 21.4 °C): $\delta_C = 169.70$, 159.93, 152.27, 152.09, 140.64, 136.41, 134.63, 133.22, 131.46, 127.73, 120.23, 117.03, 116.50, 114.13, 113.07, 100.40, 100.32, 100.19, 99.97, 99.39, 91.33, 85.27, 82.71, 82.36, 82.20-82.02 (several peaks overlapped), 81.82, 81.71, 81.52, 81.37, 81.32, 81.18, 80.73, 80.65, 80.55, 77.20, 72.79, 72.42, 72.06, 71.63-71,37 (several peaks overlapped), 71.19, 70.89, 70.80, 70.46, 70.41, 70.15, 66.82, 61.73-61.61 (several peaks overlapped), 61.44, 59.53, 59.12-59.10(several peaks overlapped), 58.95, 58.78, 57.93-57.84 (several peaks overlapped), 57.68, 57.63, 33.33, 24.79, 16.30; ESI-TOF-HRMS: (*m/z*) 1212.8654 ($[M\cdot 3Na]^{3+}$, $C_{170}H_{256}N_4O_{76}Na_3$, Calcd. 1212.8656).

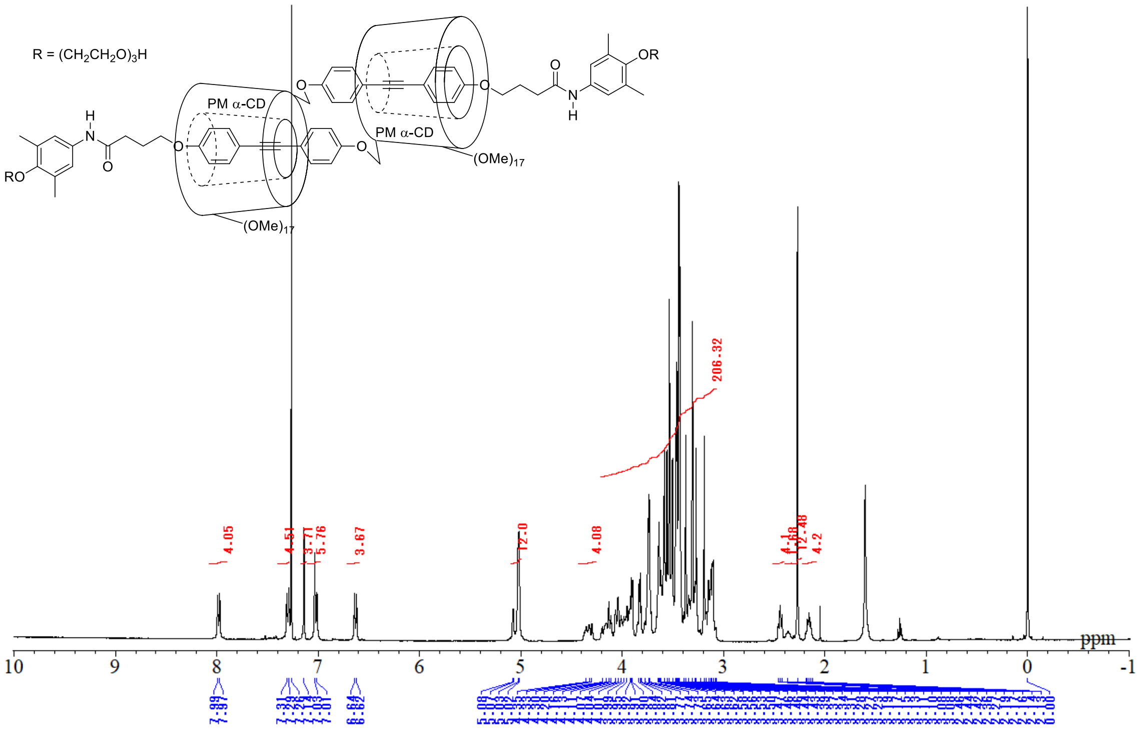


Figure S12. ^{1}H NMR spectrum of [*c*2]daisy chain rotaxane **2a**.

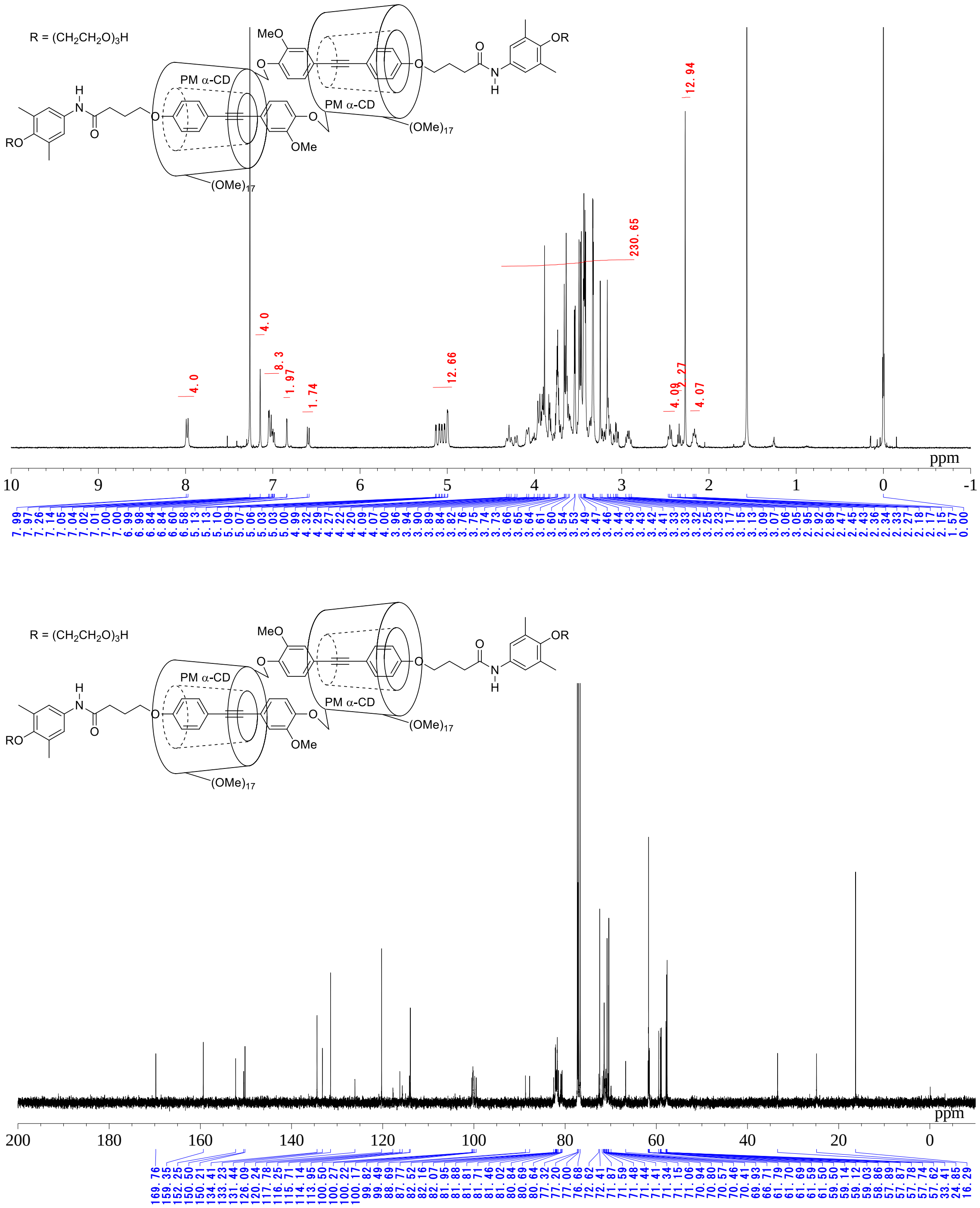


Figure S13. ^{1}H and ^{13}C NMR spectra of [*c*2]daisy chain rotaxane **2b**.

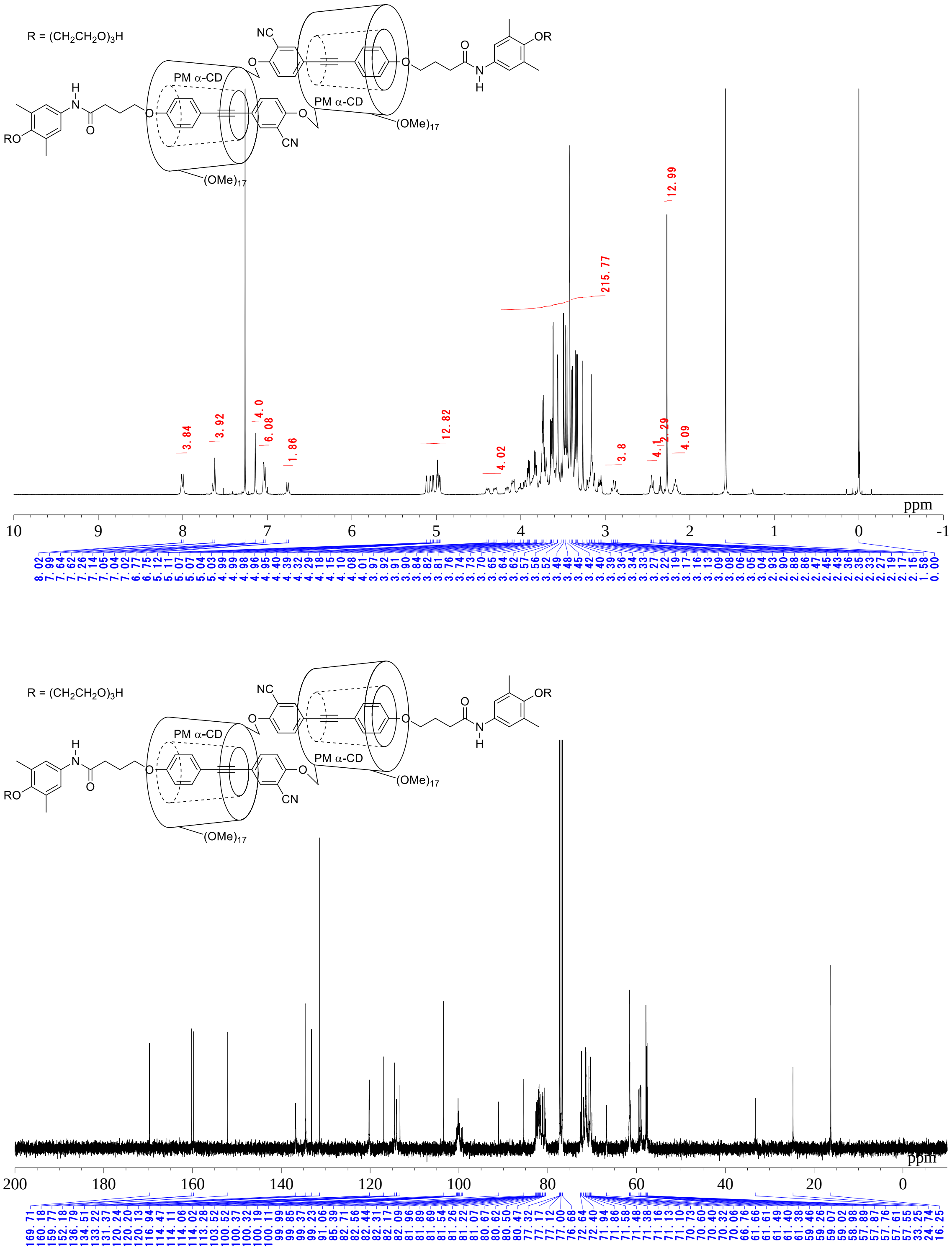


Figure S14. ^{1}H and ^{13}C NMR spectra of [*c*2]daisy chain rotaxane **2c**.

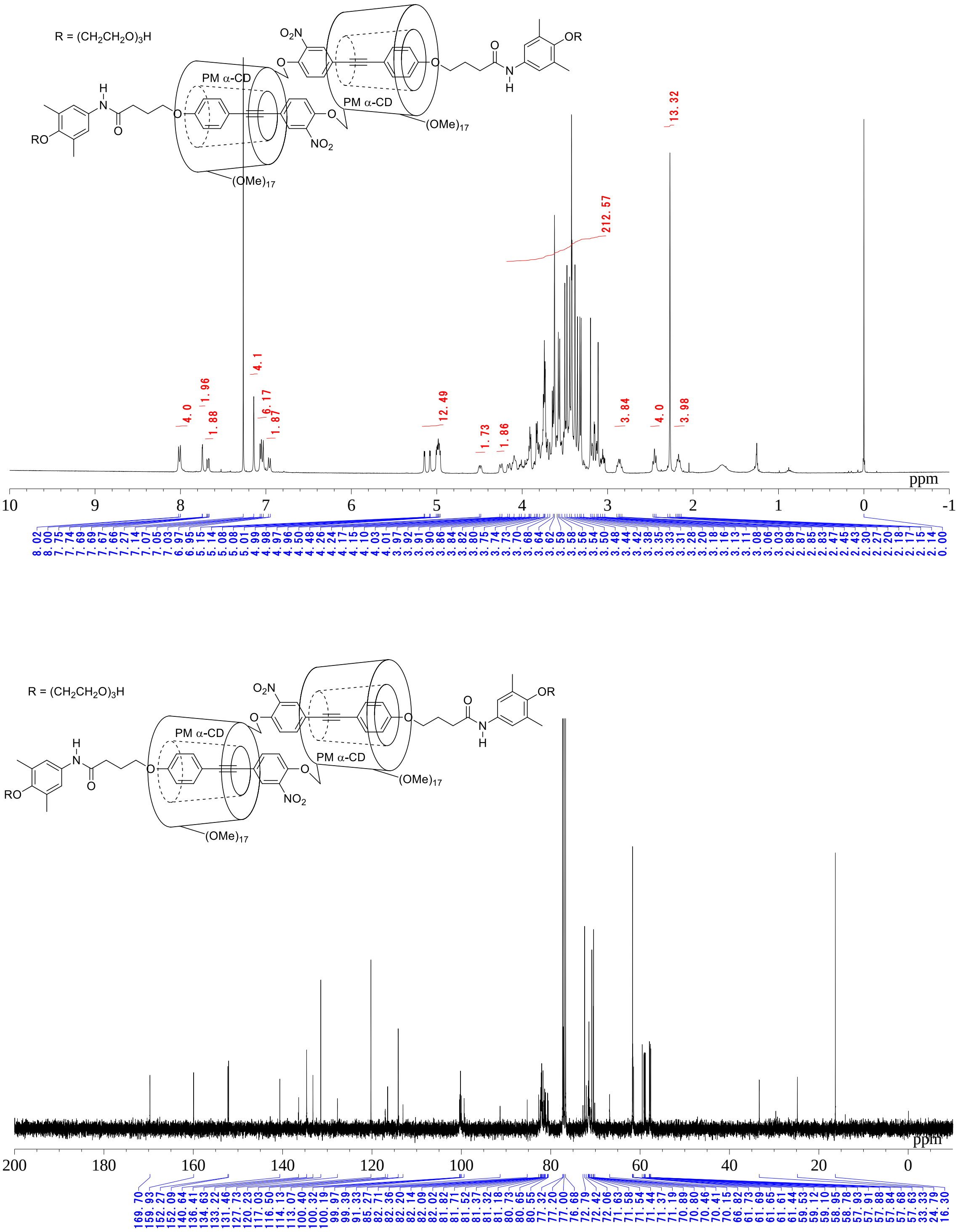
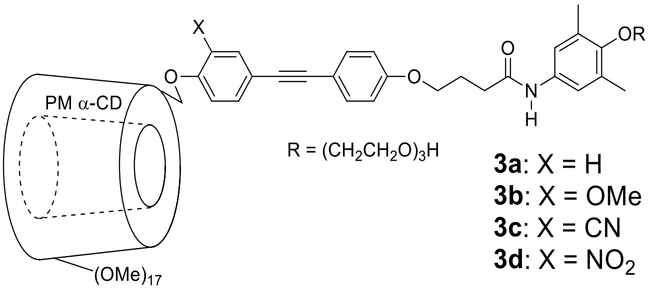


Figure S15. ^{1}H and ^{13}C NMR spectra of [*c*2]daisy chain rotaxane **2d**.

6-5. Stoppered monomer **3**



3a: X = H
3b: X = OMe
3c: X = CN
3d: X = NO_2

General Procedure

Monomer **1c** (201 mg, 0.13 mmol) and 4-{2-[2-(2-hydroxyethoxy)ethoxy]ethoxy}-3,5-dimethylaniline (149 mg, 0.55 mmol) were dissolved in CH_2Cl_2 (3.0 mL). 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl) (102 mg, 0.53 mmol) was added to the solution. The reaction mixture was stirred at room temperature for 19 h. The reaction mixture was acidified with 2 mol/L HClaq., diluted with EtOAc and washed with brine. The organic layer was separated and dried over $MgSO_4$. The solvents was removed *in vacuo*, and the residue was purified by preparative GPC (Columns: JAIGEL-1H and 2H, Eluent: $CHCl_3$). The fractions including desired stoppered monomer **3c** was concentrated *in vacuo* to yield **3c** as a white solid (150 mg, 64%).

3a: 46%; This compound was previously reported. [s2] ^{1}H NMR spectrum was shown in Figure S16.
3b: 50%; m.p.: 102-105 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 20.8 °C): δ_H = 7.42 (d, J = 8.8 Hz, 2H), 7.11 (s, 2H), 7.06-7.04 (m, 2H), 7.01 (d, J = 1.8 Hz, 1H), 6.90 (d, J = 8.4 Hz, 1H), 6.86 (d, J = 8.8 Hz, 2H), 5.12-5.01 (m, 6H), 4.50 (d, J = 9.8 Hz, 1H), 4.30 (dd, J = 5.6, 10.6 Hz, 1H), 4.12-3.12 (m, 102H), 2.55 (t, J = 7.2 Hz, 2H), 2.36 (brs, 1H), 2.26-2.20 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, 20.4 °C): δ_C = 170.32, 158.60, 152.19, 149.12, 148.65, 133.23, 132.83, 131.39, 124.31, 120.37, 116.27, 115.50, 114.42, 113.49, 100.15, 100.05-99.97 (several peaks overlapped), 88.02, 87.85, 83.07, 82.33-81.95 (several peaks overlapped), 81.10-81.01 (several peaks overlapped), 77.20, 72.41, 71.39-70.95 (several peaks overlapped), 70.75, 70.68, 70.44, 70.37, 68.94, 66.77, 61.82-61.72 (several peaks overlapped), 61.65, 58.93-58.86 (several peaks overlapped), 57.75-57.69 (several peaks overlapped), 55.61, 33.58, 24.90, 16.25; ESI-TOF-HRMS: (m/z) 907.9068 ($[M·2Na]^{2+}$, $C_{86}H_{131}NO_{37}Na_2$, Calcd. 907.9092).
3c: 64%; m.p.: 104-106 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 20.5 °C): δ_H = 7.71 (d, J = 2.1 Hz, 1H), 7.65 (dd, J = 2.1, 8.8 Hz, 1H), 7.42 (d, J = 8.8 Hz, 2H), 7.11 (s, 2H), 7.04-7.00 (m, 2H), 6.87 (d, J = 8.8 Hz, 2H), 5.10-4.97 (m, 6H), 4.56 (d, J = 9.8 Hz, 1H), 4.43 (dd, J = 5.5, 10.1 Hz, 1H), 4.25 (dd, J = 5.5, 10.1 Hz, 1H), 4.10-3.12 (m, 98H), 2.55 (t, J = 7.0 Hz, 2H), 2.38 (t, J = 6.0 Hz, 1H), 2.26-2.20 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, 21.9 °C): δ_C = 170.25, 159.62, 159.07, 152.19, 136.95, 136.16, 133.21, 132.96, 131.37, 120.36, 117.07, 115.02, 114.53, 113.01, 102.46, 100.17, 100.06-100.01 (several peaks

overlapped), 99.88, 99.60, 90.01, 85.30, 82.82, 82.42, 82.23-82.09 (several peaks overlapped), 81.96-81.93 (several peaks overlapped), 81.77, 81.22-81.16 (several peaks overlapped), 80.93, 77.20, 72.38, 71.38, 71.16-70.89 (several peaks overlapped), 70.74, 70.42, 70.36, 70.14, 66.82, 61.89, 61.82, 61.78, 61.71-61.63 (several peaks overlapped), 58.97-58.91 (several peaks overlapped), 58.85, 58.68, 57.87, 57.76, 57.69-57.65 (several peaks overlapped), 33.46, 24.84, 16.23; ESI-TOF-HRMS: (*m/z*) 905.4071 ($[M{\cdot}2Na]^{2+}$, $C_{86}H_{128}N_2O_{36}Na_2$, Calcd. 905.4016).

3d: 62%; m.p.: 107-110 °C; ^{1}H NMR (400 MHz, $CDCl_3$, 23.6 °C): δ_H = 7.95 (d, J = 2.1 Hz, 1H), 7.63 (dd, J = 2.1, 8.7 Hz, 1H), 7.42 (d, J = 8.8 Hz, 2H), 7.12-7.10 (m, 3H), 7.03 (s, 1H), 6.87 (d, J = 8.8 Hz, 2H), 5.11-4.97 (m, 6H), 4.51 (d, J = 3.0 Hz, 2H), 4.19 (m, 1H), 4.08 (t, J = 5.9 Hz, 2H), 3.99-3.11 (m, 96H), 2.55 (t, J = 7.0 Hz, 2H), 2.35 (t, J = 6.2 Hz, 1H), 2.26-2.20 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$, 19.7 °C): δ_C = 170.25, 159.11, 152.15, 151.27, 139.76, 136.36, 133.21, 133.00, 131.36, 127.94, 120.35, 116.51, 114.97, 114.53-114.39 (several peaks overlapped), 100.06-99.87 (several peaks overlapped), 99.48, 90.22, 85.21, 82.52, 82.17-81.78 (several peaks overlapped), 81.13-80.89 (several peaks overlapped), 77.19, 72.37, 71.37, 71.07-70.96 (several peaks overlapped), 70.73, 70.41-70.35 (several peaks overlapped), 66.81, 61.88-61.59 (several peaks overlapped), 58.94-58.82 (several peaks overlapped), 58.69, 57.77-57.67 (several peaks overlapped), 33.46, 24.82, 16.23; ESI-TOF-HRMS: (*m/z*) 915.3995 ($[M{\cdot}2Na]^{2+}$, $C_{85}H_{128}N_2O_{38}Na_2$, Calcd. 915.3965).

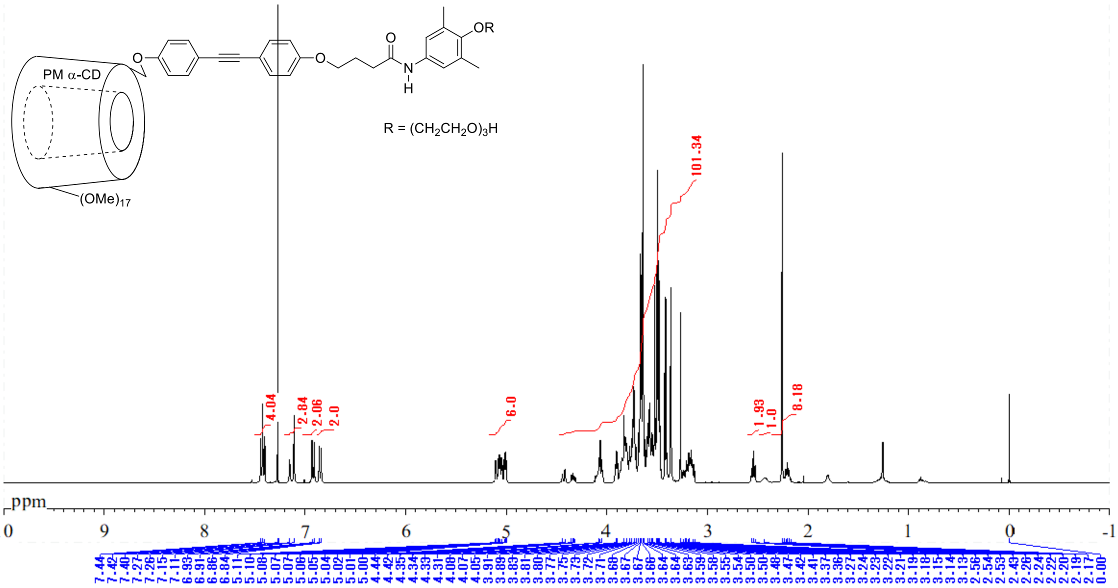


Figure S16. ^{1}H NMR spectrum of stoppered monomer **3a**.

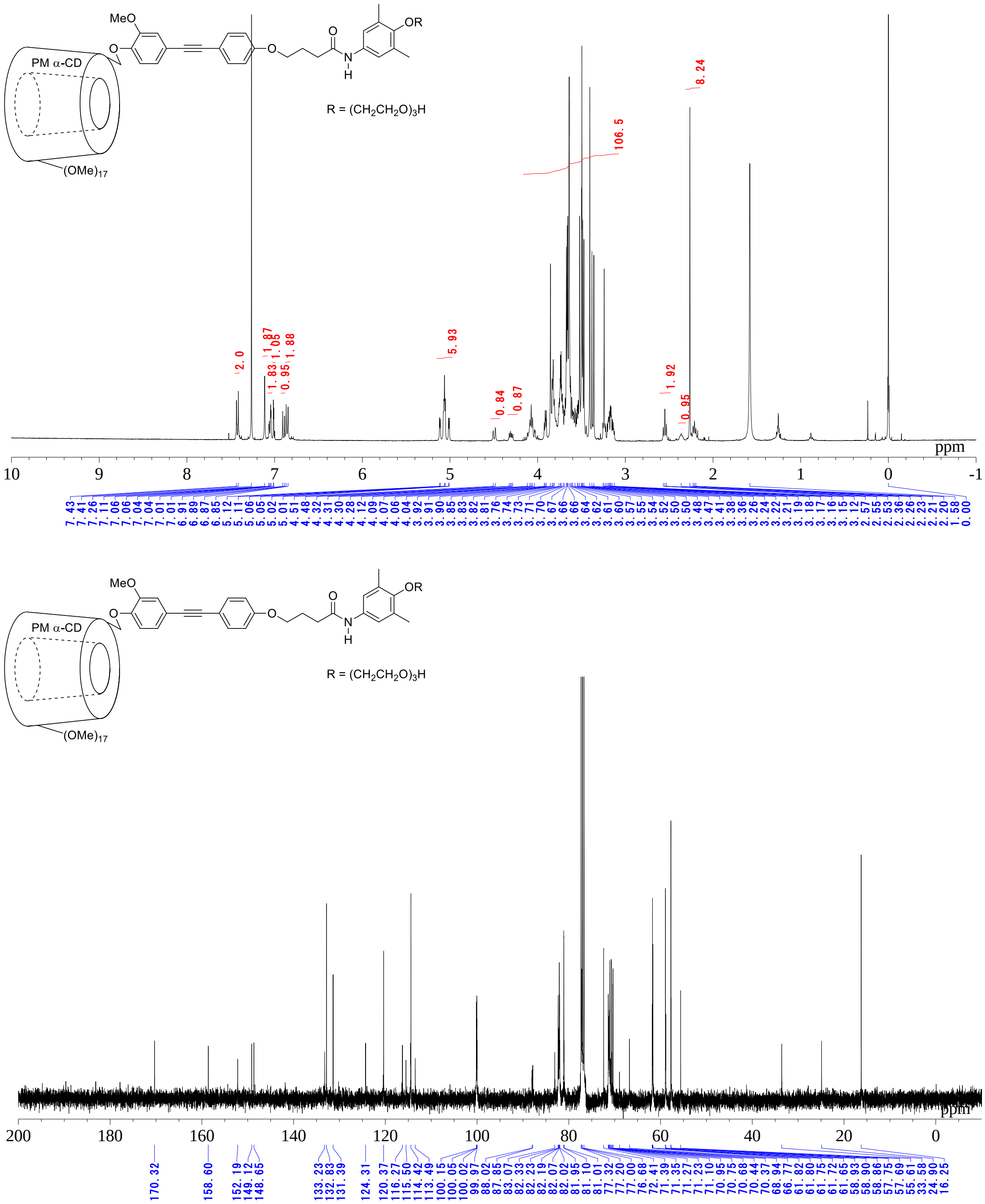


Figure S17. ^{1}H and ^{13}C NMR spectra of stoppered monomer **3b**.

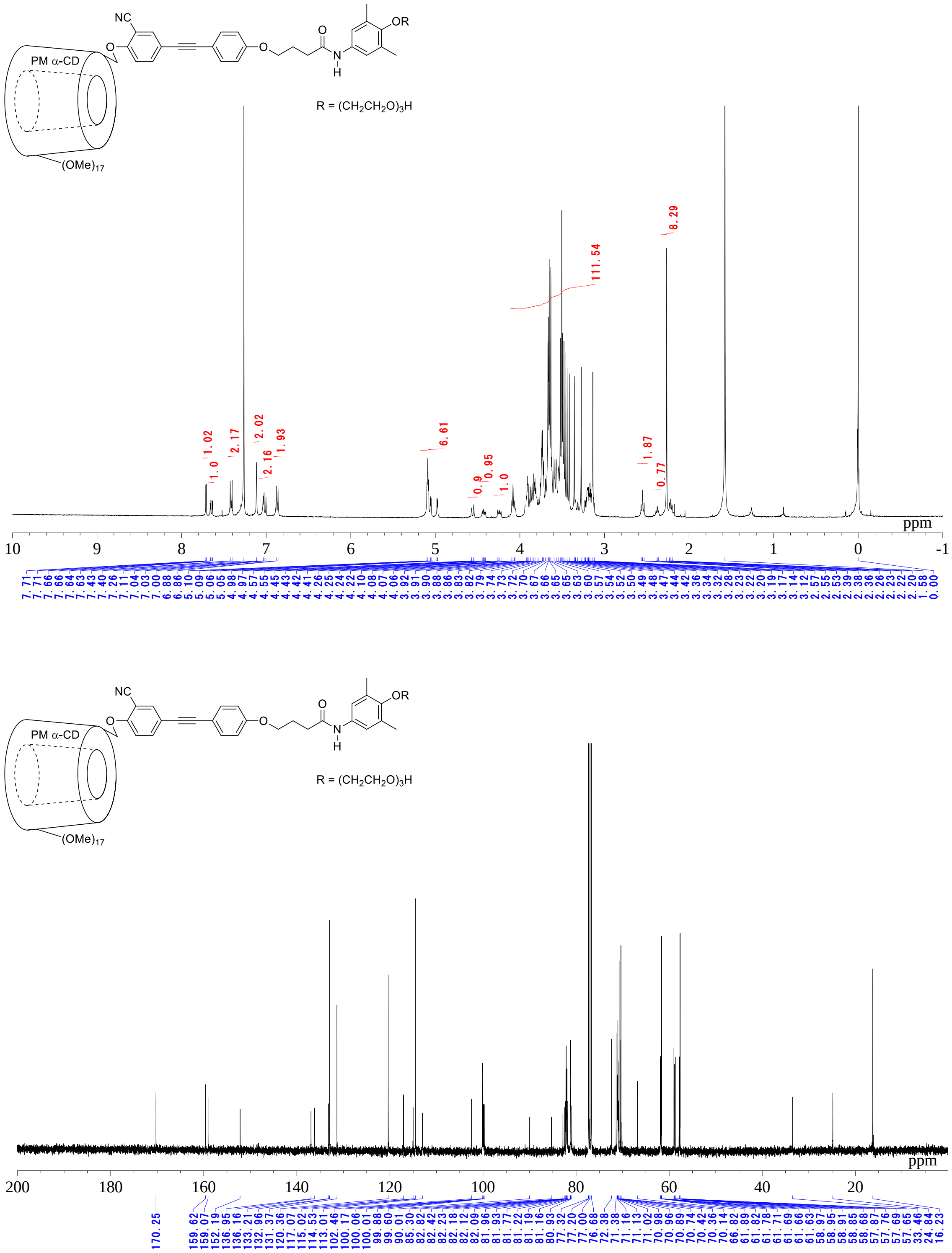


Figure S18. ^{1}H and ^{13}C NMR spectra of stoppered monomer **3c**.

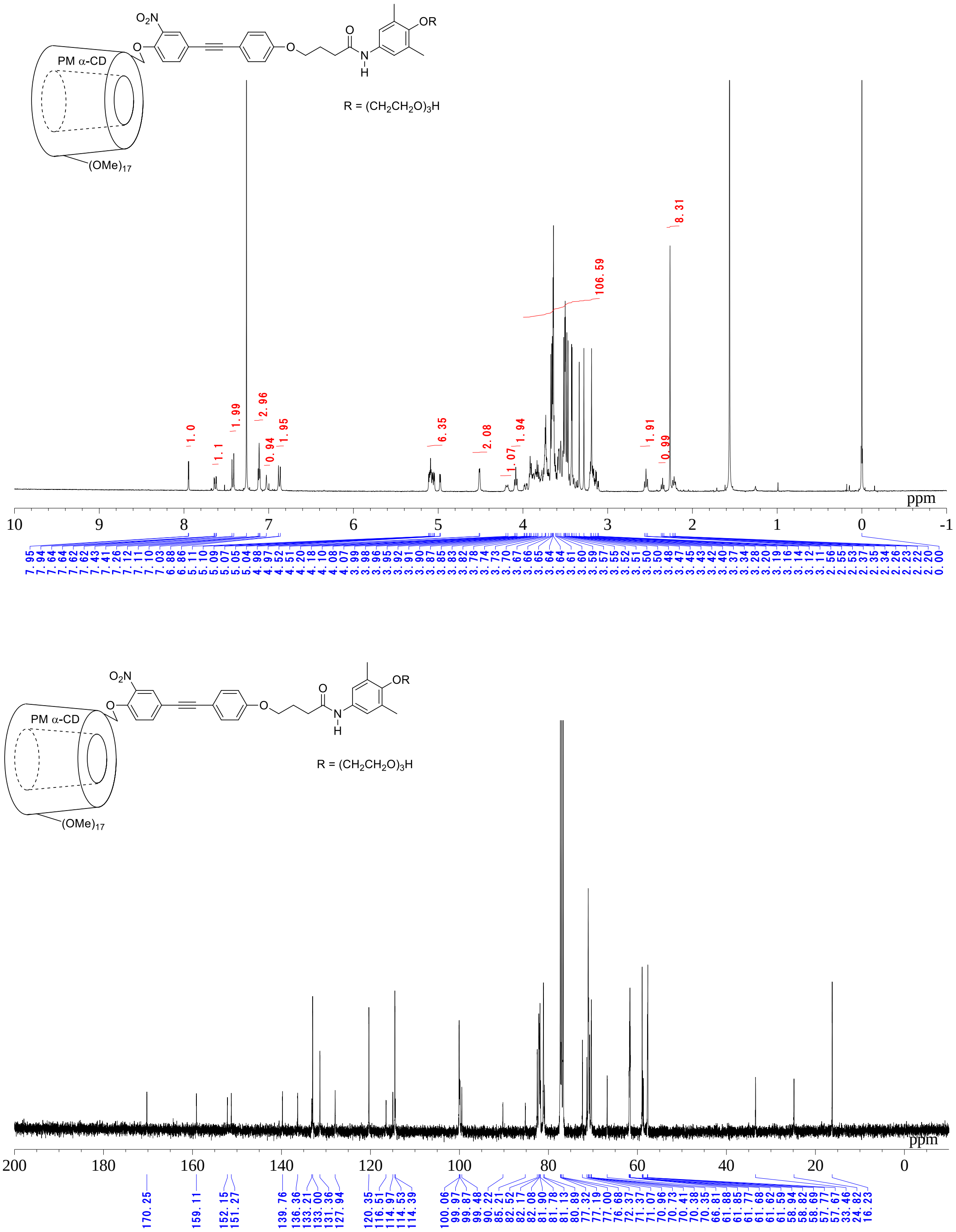


Figure S19. ^{1}H and ^{13}C NMR spectra of stoppered monomer **3d**.

7. References

[s1] T. Kaneda, T. Fujimoto, J. Goto, K. Asano, Y. Yasufuku, J. H. Jung, C. Hosono, and Y. Sakata, *Chem. Lett.* 2002, **31**, 514.

[s2] S. Tsuda, Y. Komai, S. Fujiwara, and Y. Nishiyama, *Chem. Eur. J.* 2021, **27**, 1966.