Electronic Supplementary Information (ESI)

for

Pillar[5]arene-Based [1]Rotaxane: High-Yield Synthesis, Characterization and Application in Knoevenagel Reaction

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1. Materials and methods

Materials:

4-Methoxyphenol, ethyl bromoacetate, 1,4-dimethoxybenzene, borontrifluoride diethyl etherate, paraformaldehyde were purchased from Aladin and used as received. All other commercially available reagents were used without further purification. Solvents were employed as purchased or dried according to procedures described in the literature.

Methods:

Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker AVANCE III 300 MHz spectrometer (or a Bruker 400 MHz spectrometer or a Bruker AVANCE DMX-500 spectrometer) and a Bruker 600 MHz spectrometer. Chemical shifts for proton is reported in parts per million downfield and tetramethylsilane (TMS) was used as the reference and carbon is reported in parts per million and $CDCl_3$ (77.36 ppm) was used as the reference. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration.

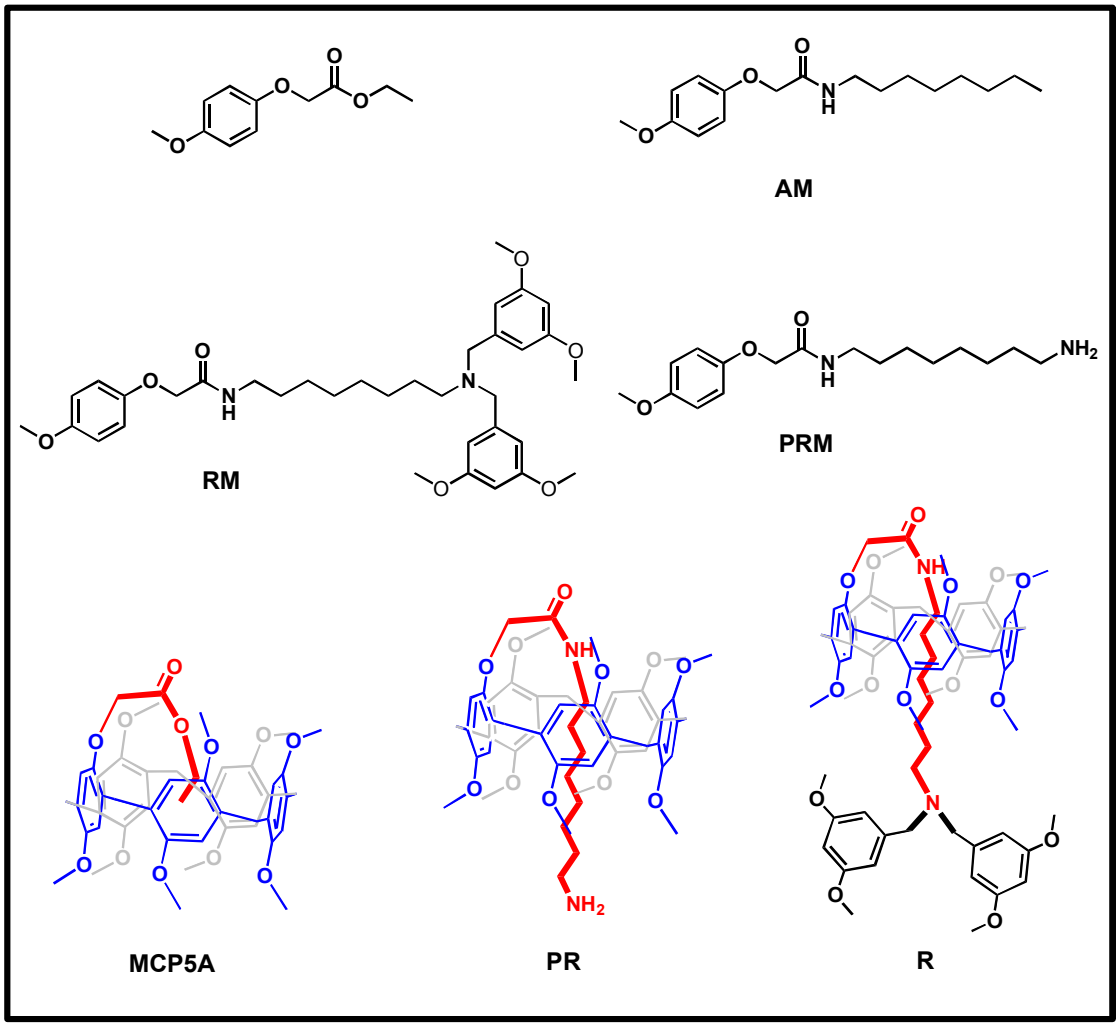
Low-resolution electrospray ionization (LR-ESI) mass spectra were obtained on a Bruker Esquire 3000 plus mass spectrometer (Bruker-Franzen Analytik GmbH Bremen, Germany) equipped with an ESI interface and an ion trap analyzer. High-resolution electrospray ionization (HRESI) mass spectra were obtained on a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). MALDI-TOF MS spectra were obtained from an autoflex TOF/TOF (Bruker, Germany) mass spectrometer, equipped with a nitrogen laser (337 nm, 3 ns pulse).

The melting points were collected on an SGW-X-4B melting point apparatus.

Thin-layered chromatography (TLC) was performed using silica gel 60 F254 plates.

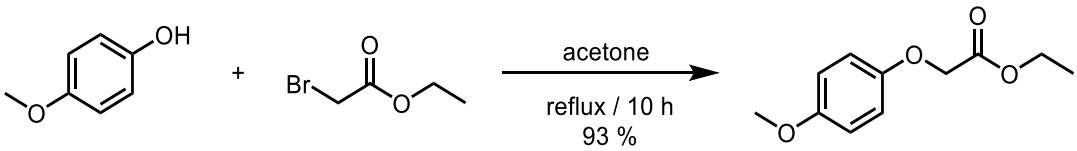
The energy-minimized structures of PR and R were optimized using the Gaussian 09 program[S1], based on the density functional theory (DFT) using the B3LYP functional and 6–31G(d) basis set. The polarizable continuum model (PCM)[S2] was employed to simulate the solvent effect in chloroform solution.

2. Synthesis and characterization of compounds



Related compounds in this work

1) Synthesis of ethyl-4-methoxy phenoxy acetate



To a solution of *p*-methoxyphenol (6.2 g, 50 mmol) and ethyl bromoacetate (8.4 g, 50 mmol) in acetone (150 mL) was added K_2CO_3 (10.5 g, 75 mmol), then the suspension was refluxed for 12 hours (monitored by TLC) and stirred overnight at room temperature. The obtained yellow mixture was filtered and concentrated to a minimum volume and then subjected to column chromatography (SiO_2, PE : EA = 10 : 1) to get the final product as colorless liquid (9.8 g, 93%). ^{1}H NMR (500 MHz, $CDCl_3$, 298K) δ 6.99 – 6.69 (m, 4H), 4.57 (s, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.76 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$, 298K) δ 169.6, 154.9, 152.4, 116.2, 115.0, 66.7, 61.6, 56.0, 14.5.

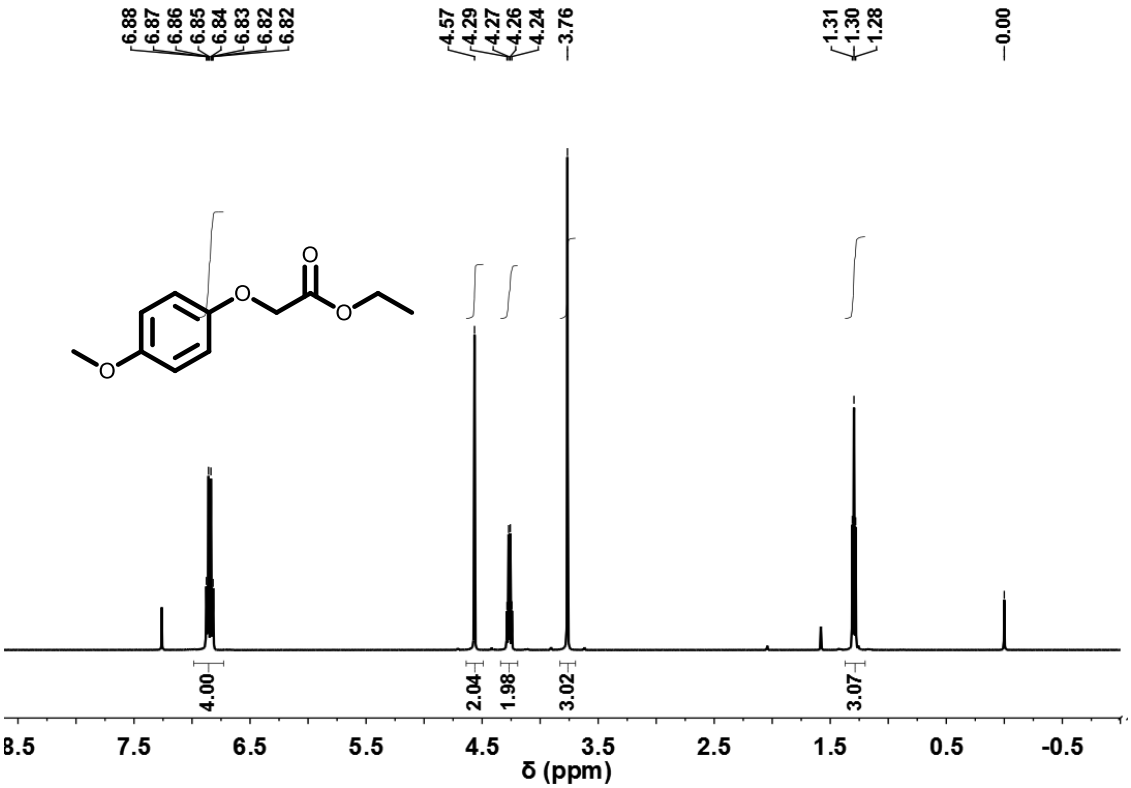


Figure S1. ^{1}H NMR spectrum of ethyl-4-methoxy phenoxy acetate.

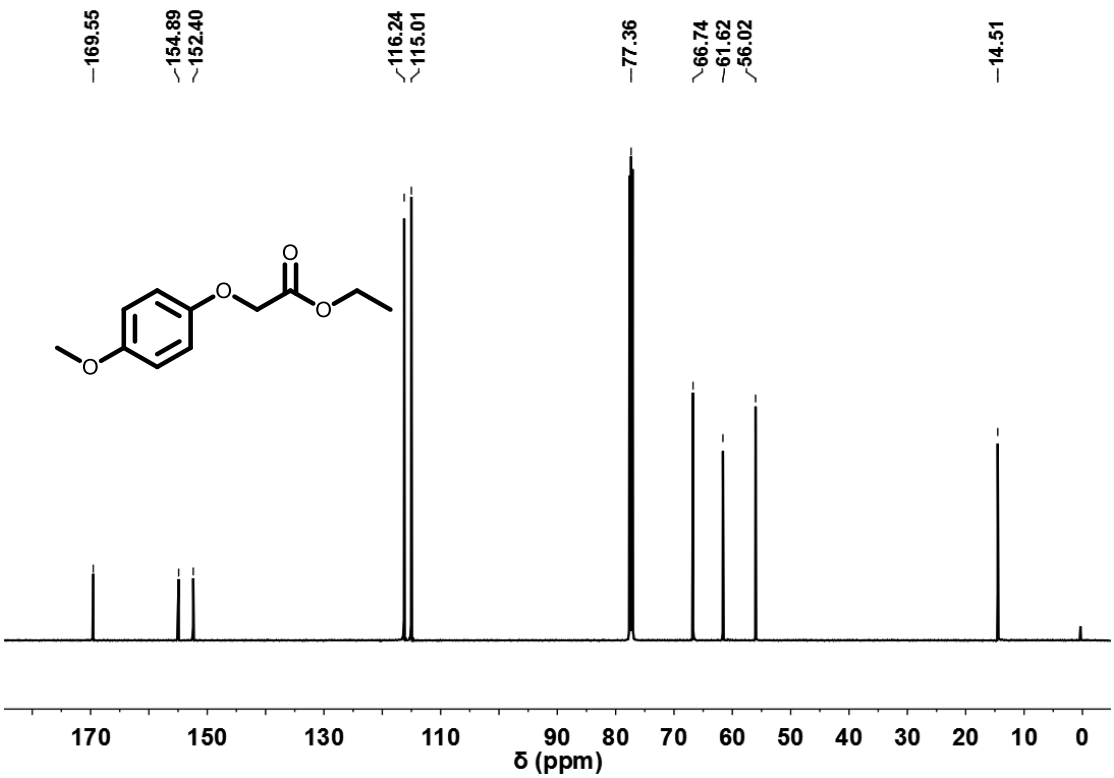
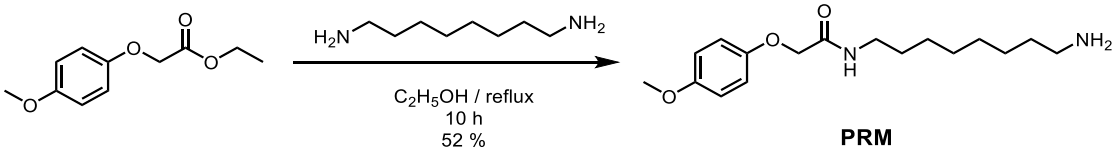


Figure S2. ^{13}C NMR spectrum of ethyl-4-methoxy phenoxy acetate.

2) Synthesis of PRM



To a solution of ethyl-4-methoxy phenoxy acetate (420 mg, 2.0 mmol) in ethanol (5.0 mL) was added 1,8-diaminooctane (577 mg, 4.0 mmol). After keeping the reaction mixture at reflux for 12 hours, the solvent was removed on rotor-vap. The crude product was purified by column chromatography (SiO_2, DCM : MeOH = 10 : 1) to give a white powder (321 mg, 52 %). ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 6.85 (s, 4H), 6.60 (s, 1H), 4.43 (s, 2H), 3.78 (s, 3H), 3.33 (q, *J* = 6.7 Hz, 2H), 2.68 (t, *J* = 7.0 Hz, 2H), 1.55 (s, 4H), 1.45 (dd, *J* = 15.4, 9.2 Hz, 2H), 1.28 (d, *J* = 17.6 Hz, 8H). ^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 168.6, 155.0, 151.7, 115.9, 115.1, 68.5, 56.0, 39.3, 33.9, 29.9, 29.7, 29.5, 27.1. LC-ESI-MS: m/z calcd for $[M+H]^+$ (100.00 %) $C_{17}H_{29}N_2O_3^+$, 309.217; found 309.213.

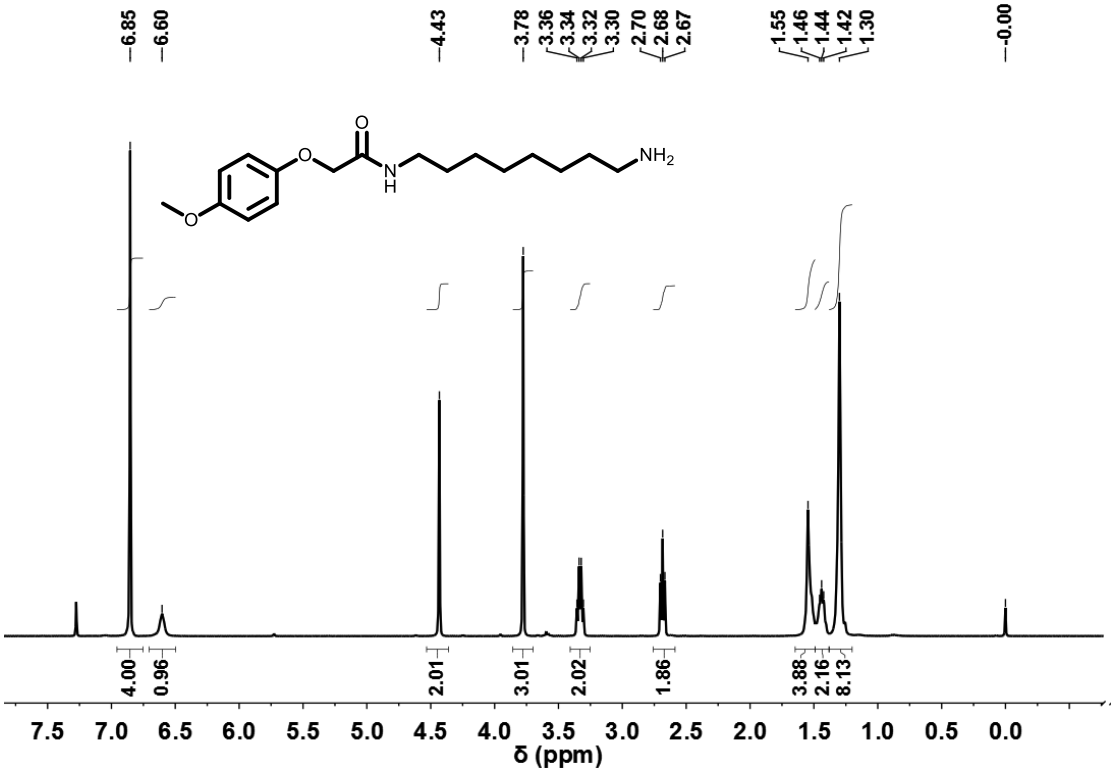


Figure S3. ^{1}H NMR spectrum of **PRM**.

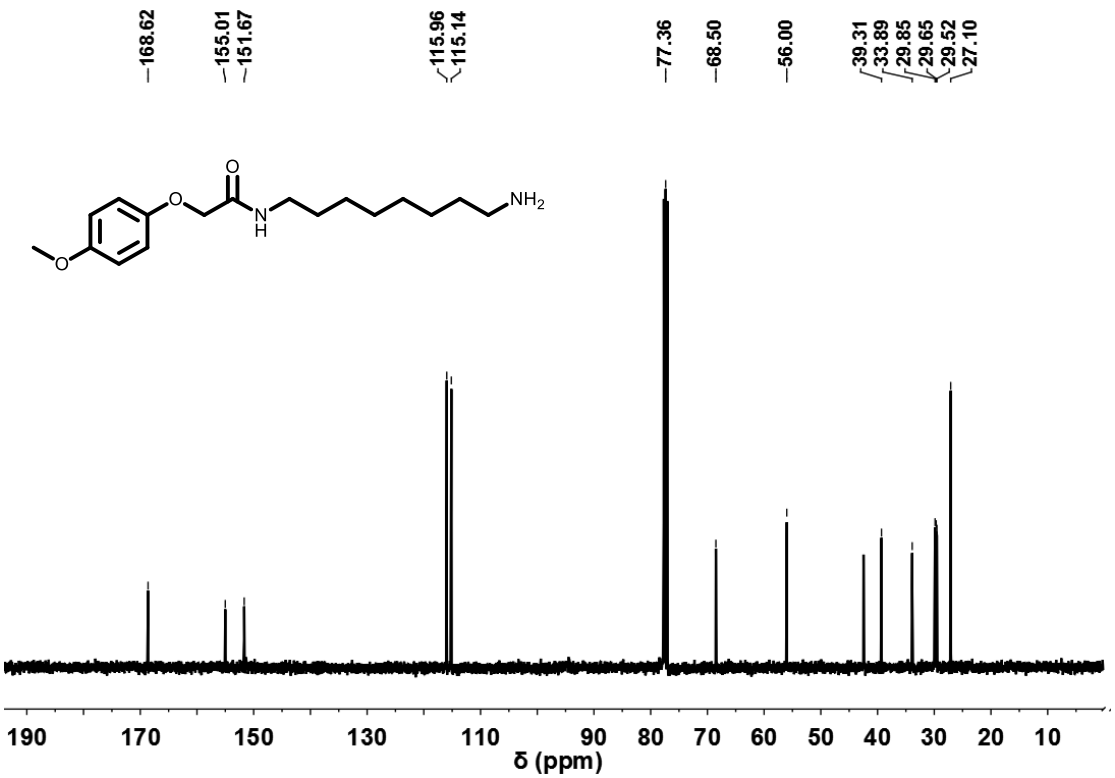


Figure S4. ^{13}C NMR spectrum of **PRM**.

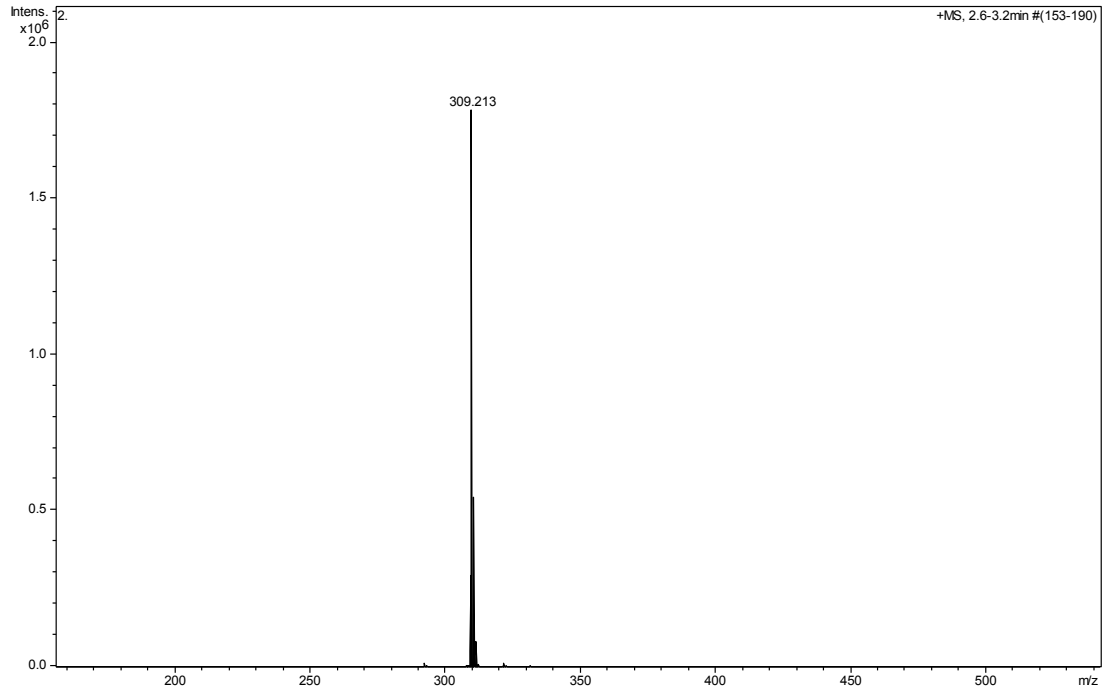
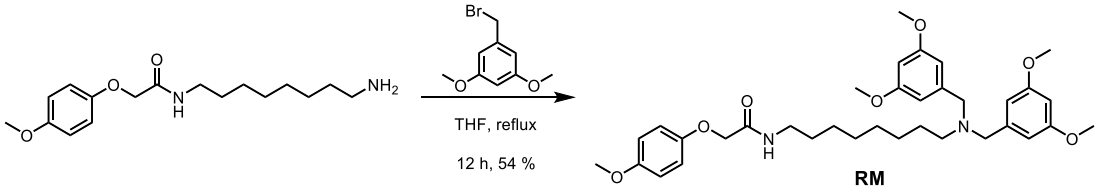


Figure S5. Mass spectrum of **PRM**. LC-ESI-MS: m/z calculated for $[M+H]^+$ (100.00 %) $C_{17}H_{29}N_2O_3^+$, 309.217; found 309.213.

3) Synthesis of RM



To a solution of **PRM** (198.5 mg, 0.66 mmol) in THF (3.0 mL) was added 1-(bromomethyl)-3,5-dimethoxybenzene (327.1 mg, 1.46 mmol). The mixture was refluxed for 12 hours, and then the solvent was removed on rotor-vap. After purifying by column chromatography (SiO_2, DCM : MeOH = 40 : 1), the final product was collected for analysis (211.6 mg, 54 %). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) δ 6.85 (s, 4H), 6.56 (d, *J* = 1.8 Hz, 4H), 6.33 (s, 2H), 4.43 (s, 2H), 3.90 – 3.68 (m, 15H), 3.49 (s, 3H), 3.31 (dd, *J* = 13.6, 6.8 Hz, 2H), 2.41 (t, *J* = 7.2 Hz, 2H), 1.50 (dd, *J* = 13.8, 6.8 Hz, 4H), 1.24 (dd, *J* = 33.3, 11.6 Hz, 8H). ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) δ 168.7, 161.0, 155.1, 151.8, 143.1, 120.0, 116.0, 115.2, 106.8, 99.1, 68.6, 58.8, 56.0, 55.6, 39.4, 29.9, 29.7, 29.6, 27.6, 27.4, 27.2.

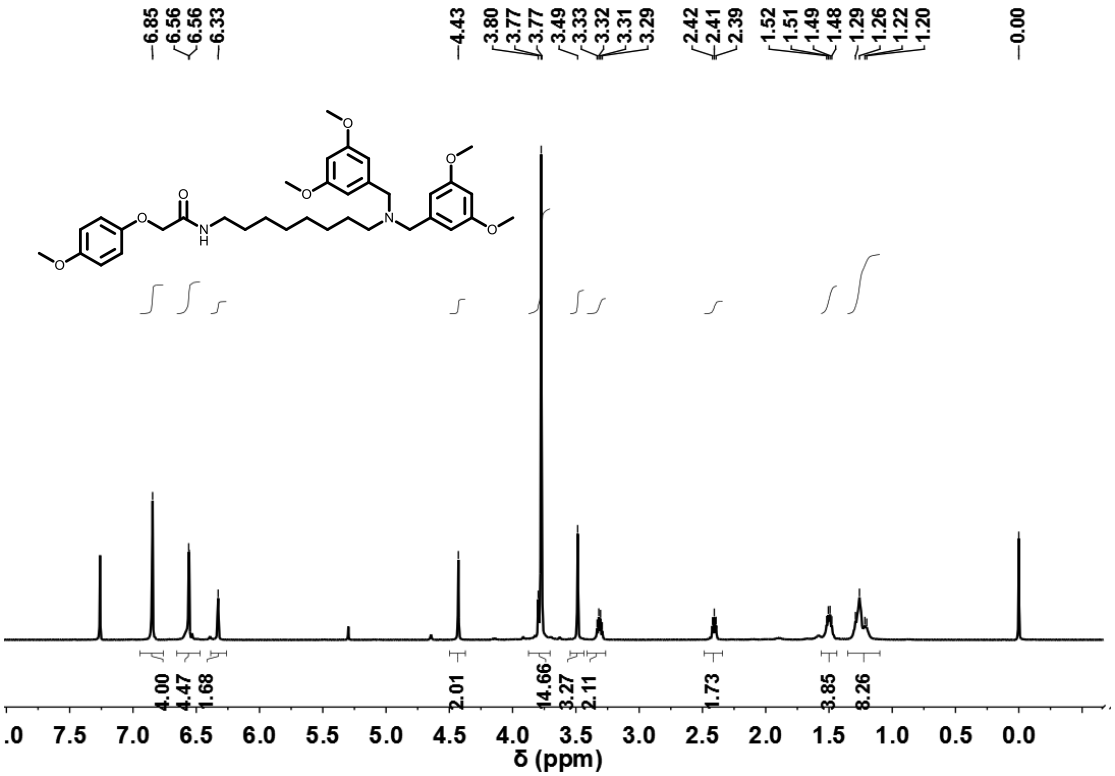


Figure S6. ^{1}H NMR spectrum of **RM**.

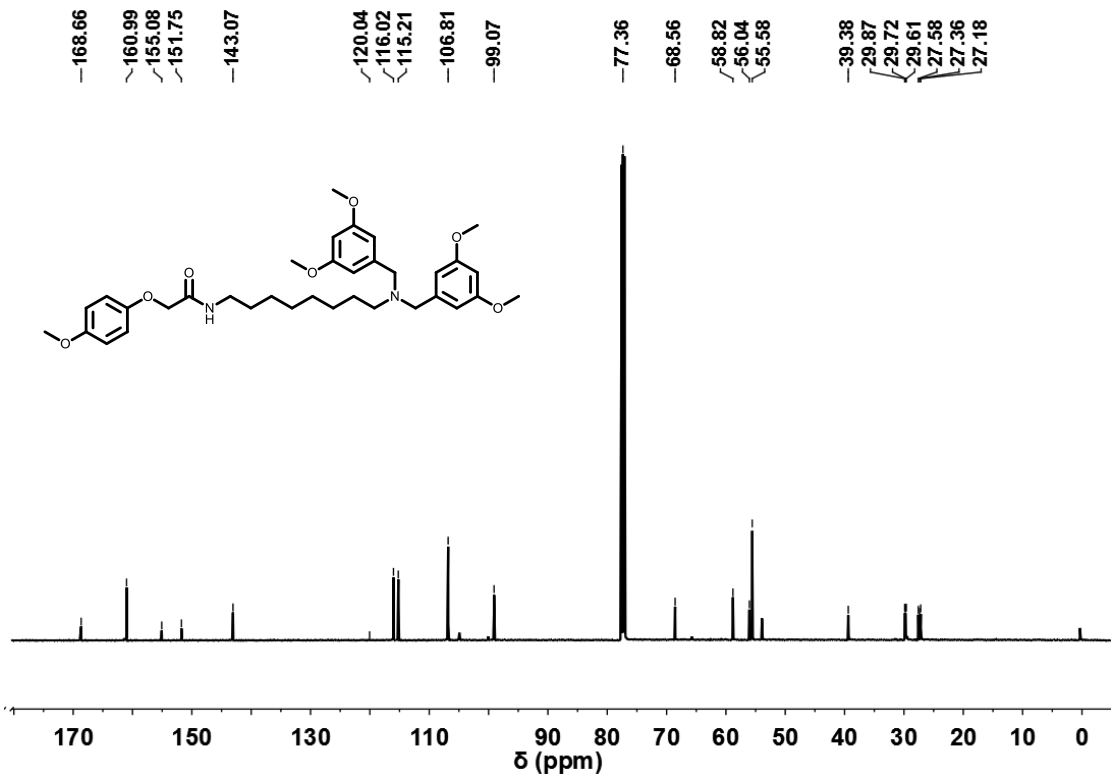


Figure S7. ^{13}C NMR spectrum of **RM**.

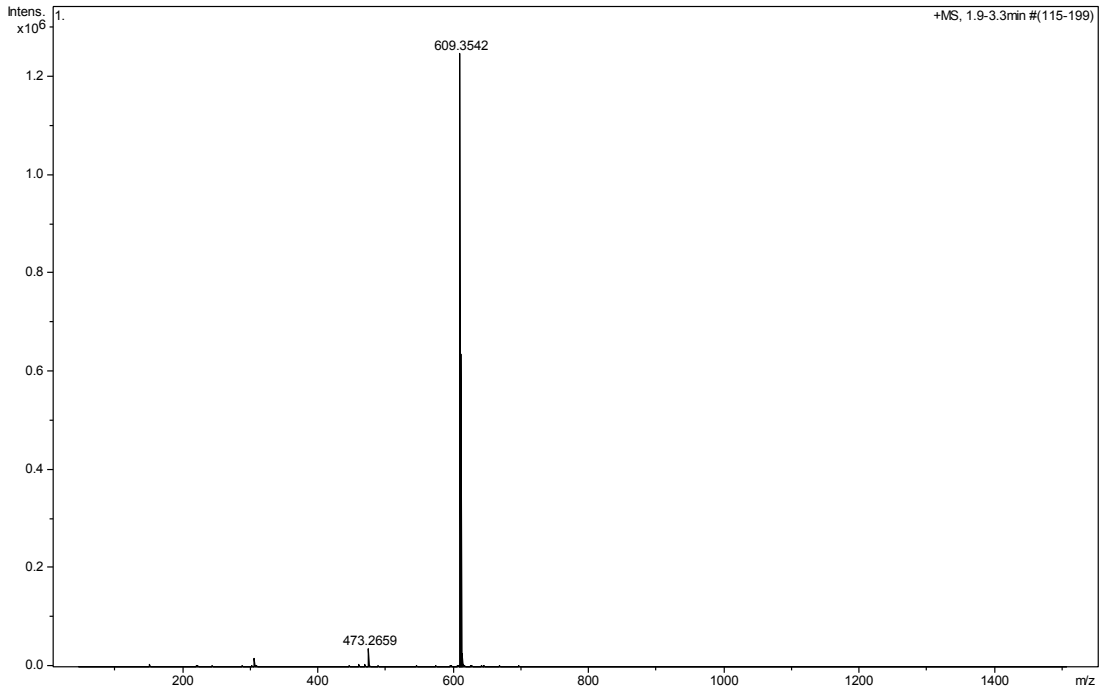
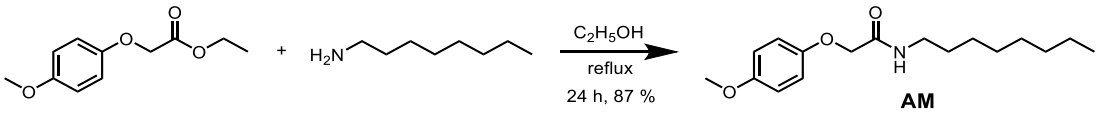


Figure S8. Mass spectrum of **RM**. LC-ESI-MS: m/z calcd for $[M+H]^+$ (100.00 %) $C_{35}H_{49}N_2O_7^+$, 609.3534; found 609.3542.

4) Synthesis of AM



To a solution of ethyl-4-methoxy phenoxy acetate (420 mg, 2.0 mmol) in ethanol (5.0 mL) was added *n*-octylamine (315.5 mg, 2.5 mmol). The mixture was refluxed for 24 hours, and then the solvent was removed on rotor-vap. After purifying by column chromatography (SiO_2, PE : EA = 10 : 1), the white powder was collected for analysis (510.5 mg, 87 %). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ 6.85 (s, 4H), 6.58 (s, 1H), 4.43 (s, 2H), 3.77 (s, 3H), 3.33 (dd, *J* = 13.6, 6.8 Hz, 2H), 1.53 (dd, *J* = 13.9, 6.9 Hz, 2H), 1.28 (dd, *J* = 14.6, 5.9 Hz, 10H), 0.88 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, 298 K) δ 168.7, 155.1, 151.7, 116.0, 115.2, 68.6, 56.0, 39.4, 32.1, 29.9, 29.5, 29.5, 27.2, 22.9, 14.4.

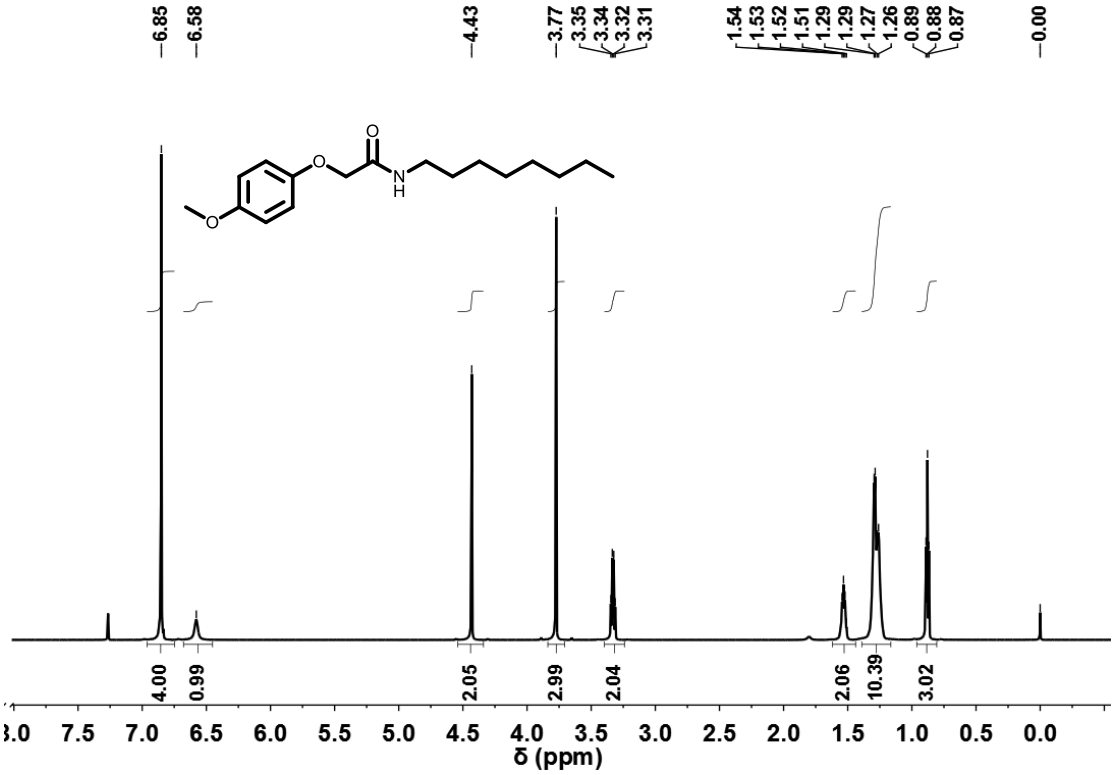


Figure S9. ^{1}H NMR spectrum of **AM**.

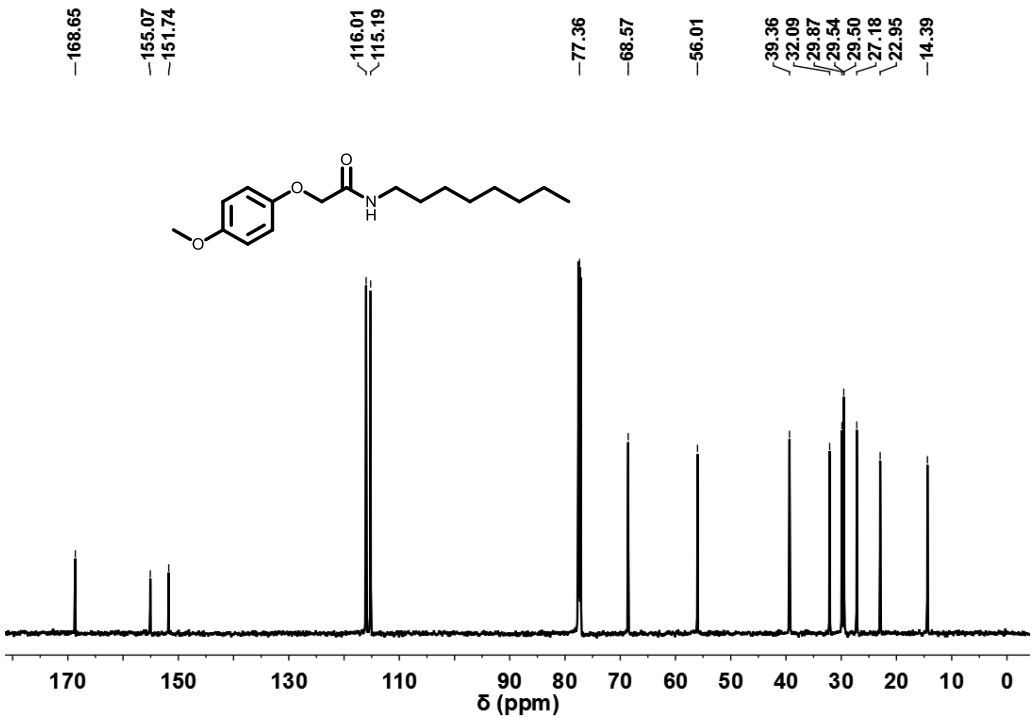


Figure S10. ^{13}C NMR spectrum of **AM**.

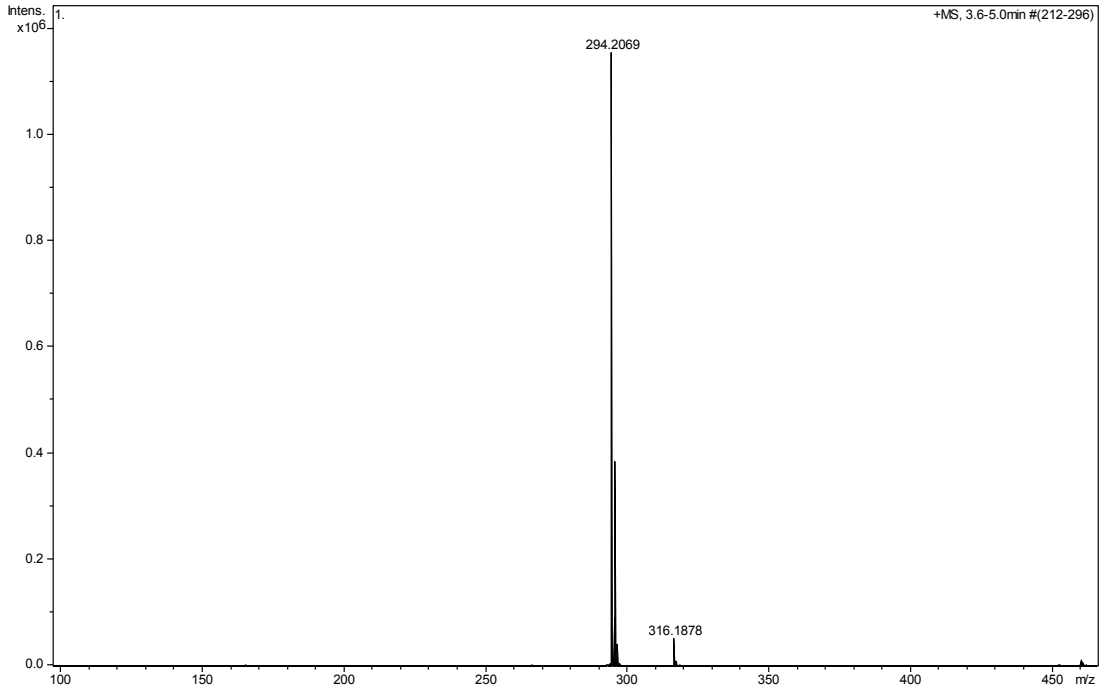
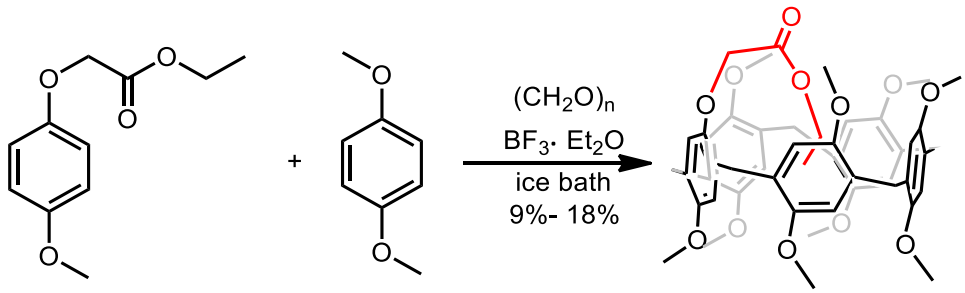


Figure S11. Mass spectrum of **AM**. LC-ESI-MS: m/z calcd for $[M+H]^+$, $C_{17}H_{28}NO_3^+$, 294.2064, found 294.2069; for $[M+Na]^+$, $C_{17}H_{27}NO_3Na^+$, 316.1883; found 316.1878.

5) Synthesis of MCP5A



MCP5A

To a solution of 1,4-dimethoxybenzene (2.76 g, 20.0 mmol) in dichloromethane (250.0 mL) was added paraformaldehyde (2.2 g, 73.0 mmol) and ethyl-4-methoxy phenoxy acetate (0.84 g, 4.0 mmol), then the suspension was stirred at room temperature for 50 minutes. Then, boron trifluoride diethyl etherate [$BF_3{\cdot}O(C_2H_5)_2$, 3.6 mL, 28.3 mmol] was added to the solution, and the mixture was stirred at room temperature for 10 minutes (monitored by TLC). The reaction was quenched with an aqueous solution of $NaHCO_3$ (200 mL). The obtained yellow mixture was filtered off and the organic phase was collected. The solvent was removed on rotor-vap and the crude product was purified by column chromatography (SiO_2, PE : DCM : EA = 50 : 20 :1) to get the final product **MCP5A** as a white powder[S3] (0.62 g, 18 %). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ 7.10 – 6.39 (m, 10H), 4.50 (s, 2H), 4.00 – 3.48 (m, 37H), 2.18 (q, *J* = 7.0 Hz, 2H), -1.46 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, 298 K) δ 169.4, 151.6, 151.2, 151.1, 150.8, 150.5, 150.3, 150.2, 150.0, 129.7, 129.5, 129.3, 129.0, 128.9, 128.8, 128.6, 128.4, 128.1, 127.5, 115.6, 115.5, 114.5, 114.4, 114.2, 113.8, 113.4, 113.0, 112.7, 65.1, 60.9, 56.8, 56.4, 56.3, 56.2, 56.0, 55.9, 55.8, 55.5, 32.2, 30.7, 30.1, 29.3, 29.0, 27.6, 11.1. m.p. 201.6-202.4 ℃. MALDI-TOF-MS: m/z calcd for $[M\text{-}H]^-$ $C_{48}H_{53}O_{12}^-$, 821.935; found 821.891.

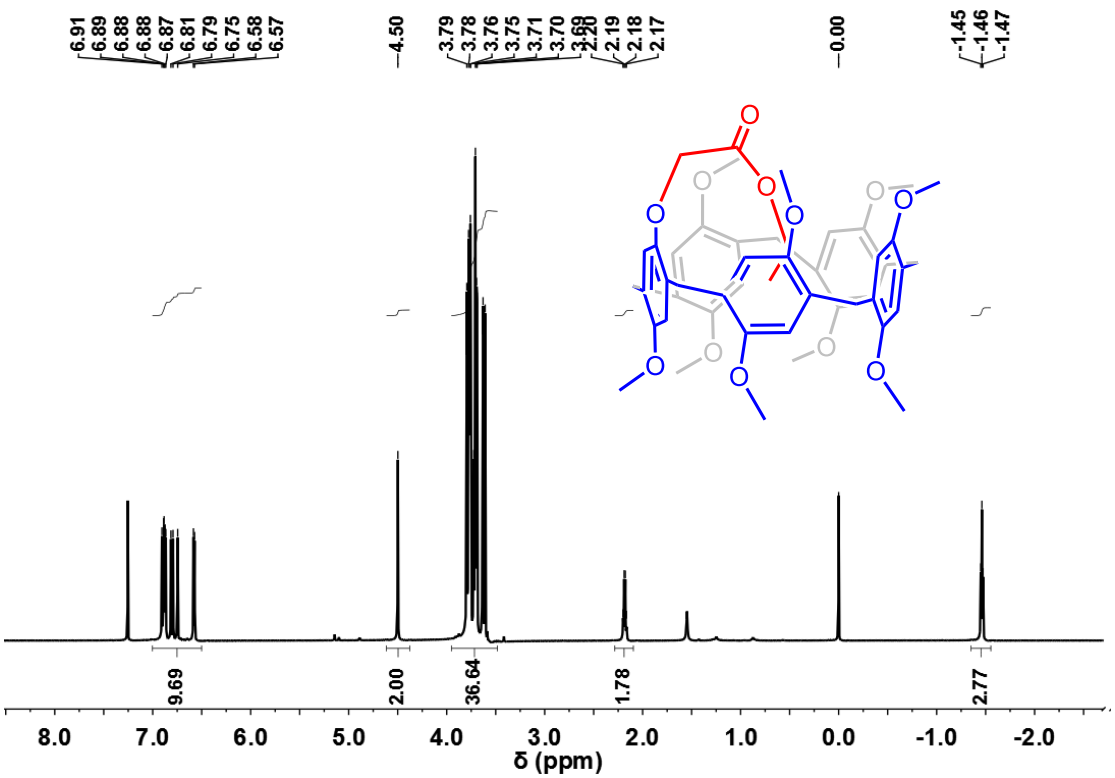


Figure S12. ^{1}H NMR spectrum of **MCP5A.**

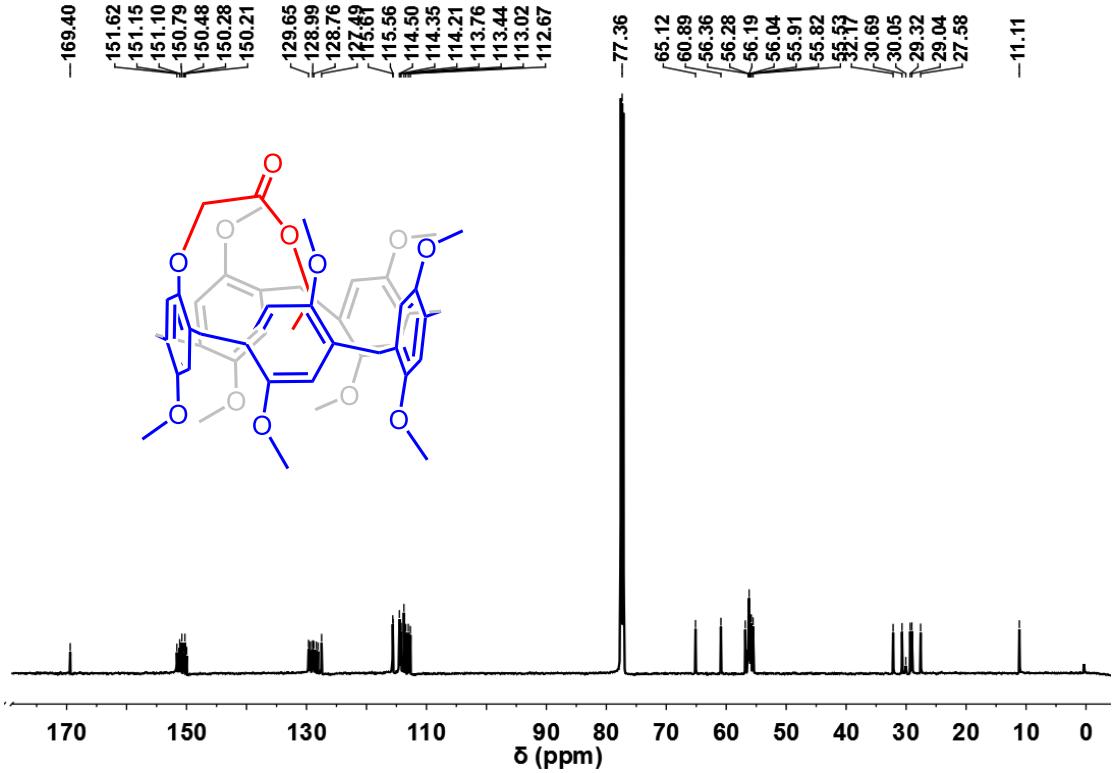


Figure S13. ^{13}C NMR spectrum of **MCP5A.**

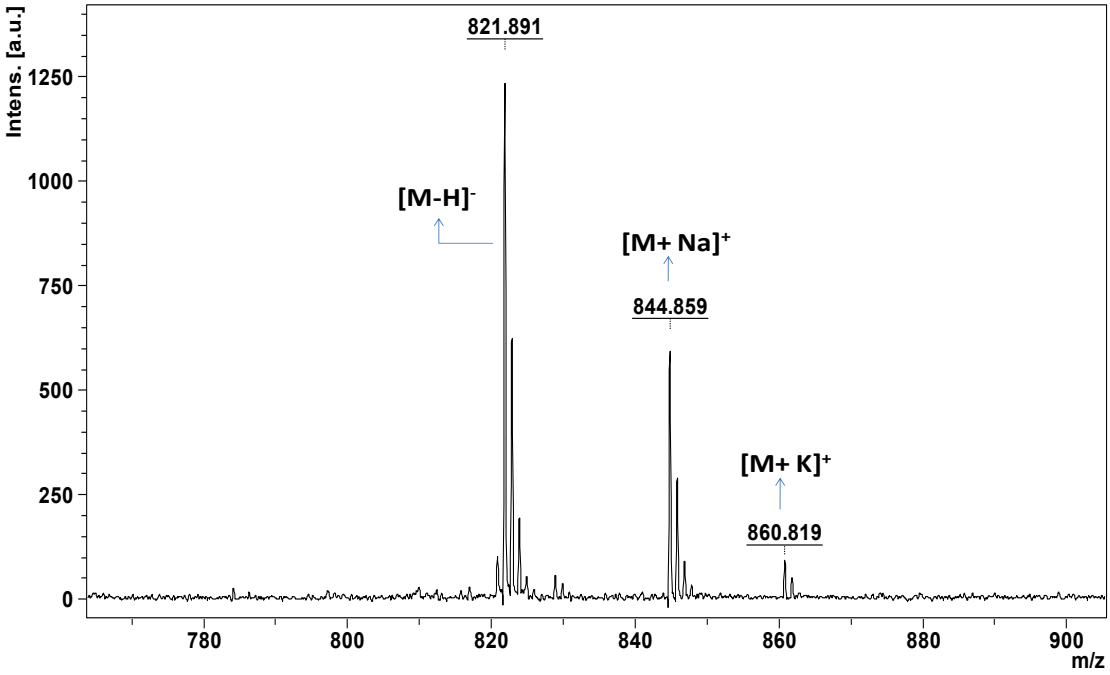
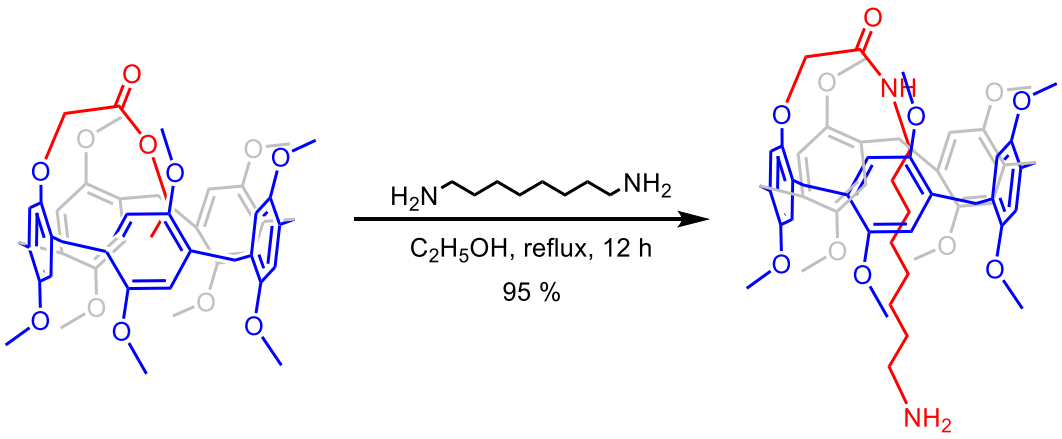


Figure S14. MALDI-TOF-MS of **MCP5A.**

6) Synthesis of PR



PR

To a 50.0 mL round-bottom flask, **MCP5A** (1.01 g, 1.22 mmol) and 1,8-diaminooctane (5.77 g, 40.0 mmol) were dissolved in 10.0 mL of C_2H_5OH. The mixture was refluxed for 24 hours, and then added 30 mL of distillated water. The suspension was filtered off and washed there times with water (3×10 mL) and then seperated by column chromatography (SiO_2, DCM : MeOH = 10 : 1), the white powder was collected for analysis (1.07 g, 95 %). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ 6.86 (ddd, J = 78.3, 45.6, 36.4 Hz, 10H), 5.23 (s, 1H), 4.57 (s, 2H), 3.75 (ddd, J = 70.7, 39.1, 27.4 Hz, 38H), 2.70 (t, J = 7.2 Hz, 2H), 2.21 (s, 2H), 1.45 – 1.10 (m, 3H), 0.67 (s, 2H), -0.13 (s, 2H), -1.07 (s, 2H), -1.39 (s, 2H), -2.17 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.71, 151.15, 151.01, 150.85, 150.69, 150.65, 150.52, 150.42, 150.38, 147.56, 114.48, 114.37, 114.29, 113.90, 113.17, 113.11, 112.95, 112.74, 66.37, 56.42, 56.20, 56.11, 55.98, 55.88, 55.84, 55.78, 55.65, 55.49, 42.69, 38.33, 34.03, 30.47, 30.01, 29.58, 29.51, 29.23, 29.00, 28.72, 28.67, 27.78, 27.11, 24.04. HRESIMS: m/z calcd for $[M+H]^+$ (100.00 %) $C_{54}H_{69}N_2O_{11}^+$, 921.4896; found 921.4920; m/z calcd for $[M+2H]^{2+}$ (22.33 %) $C_{54}H_{70}N_2O_{11}^{2+}$, 922.4969; found 922.4966. MALDI-TOF-MS: found 921.057. m.p. 172.5-173.8 ℃.

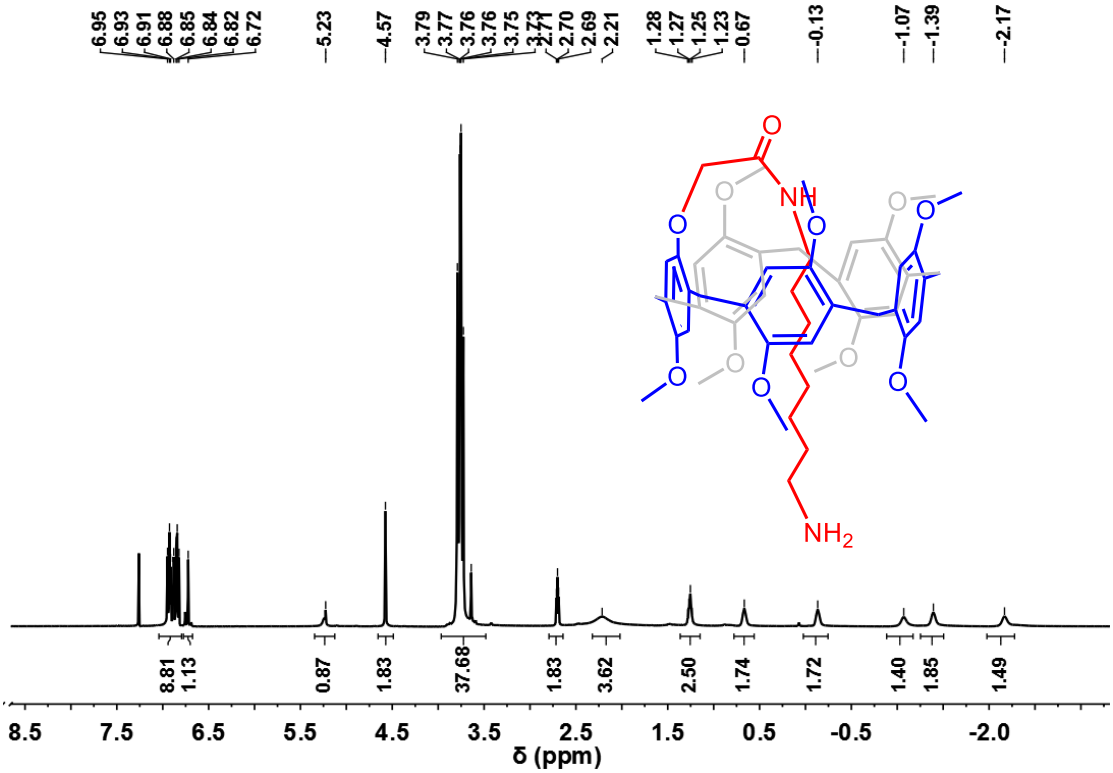


Figure S15. ^{1}H NMR spectrum of **PR.**

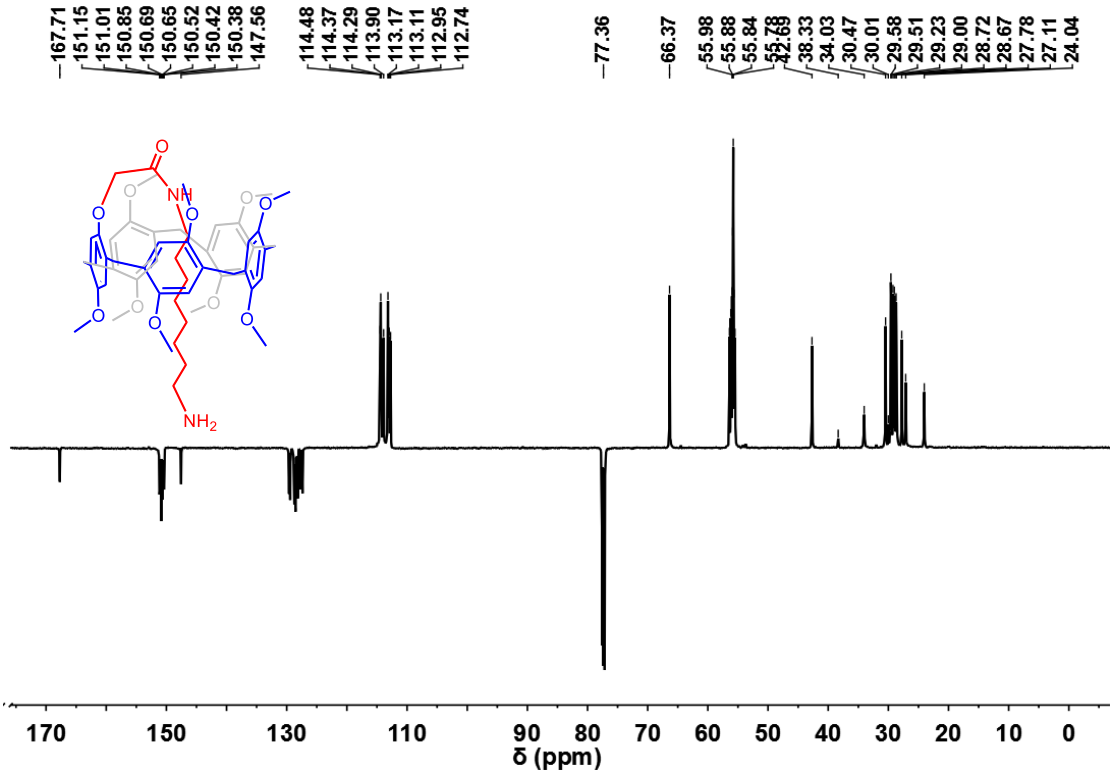


Figure S16. ^{13}C NMR spectrum of **PR.**

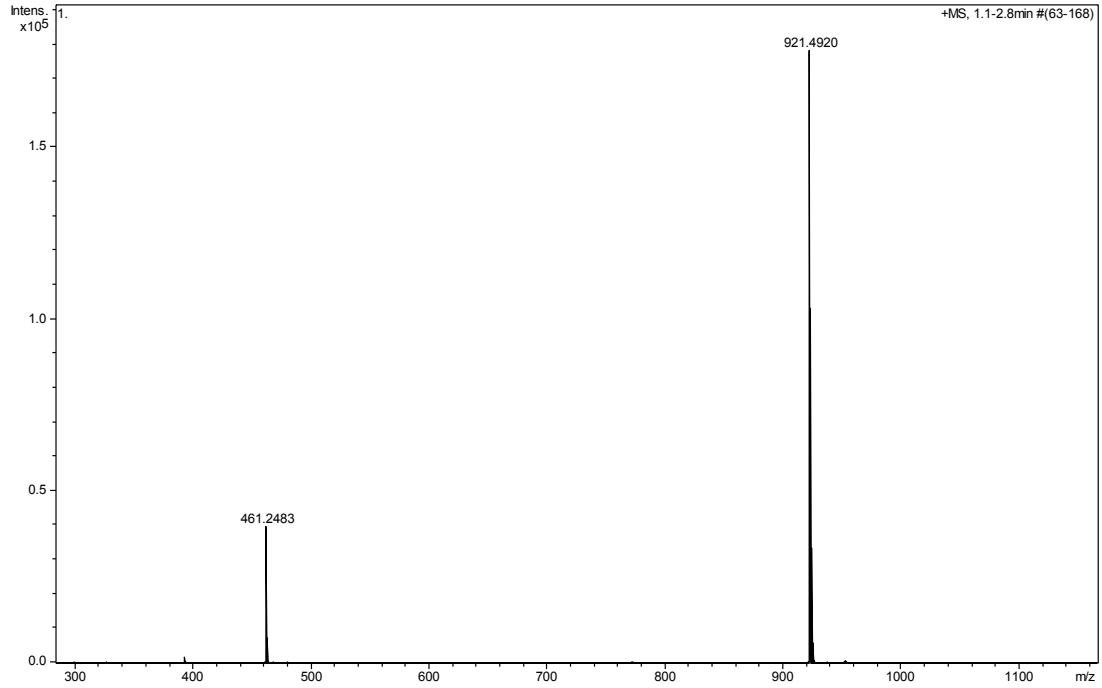


Figure S17. Mass spectrum of **PR**. HRESIMS: m/z calcd for $[M+H]^+$ (100.00 %) $C_{54}H_{69}N_2O_{11}^+$, 921.4896; found 921.4920; m/z calcd for $[M+2H]^{2+}$ (22.33 %) $C_{54}H_{70}N_2O_{11}^{2+}$, 922.4969; found 922.4966.

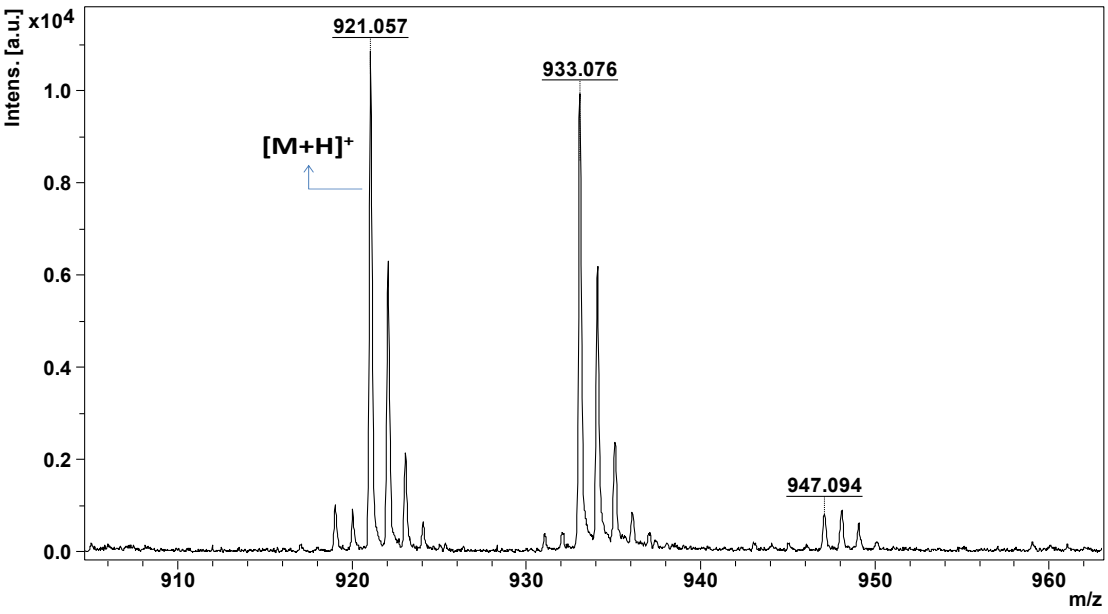


Figure S18. MALDI-TOF-MS of **PR**.

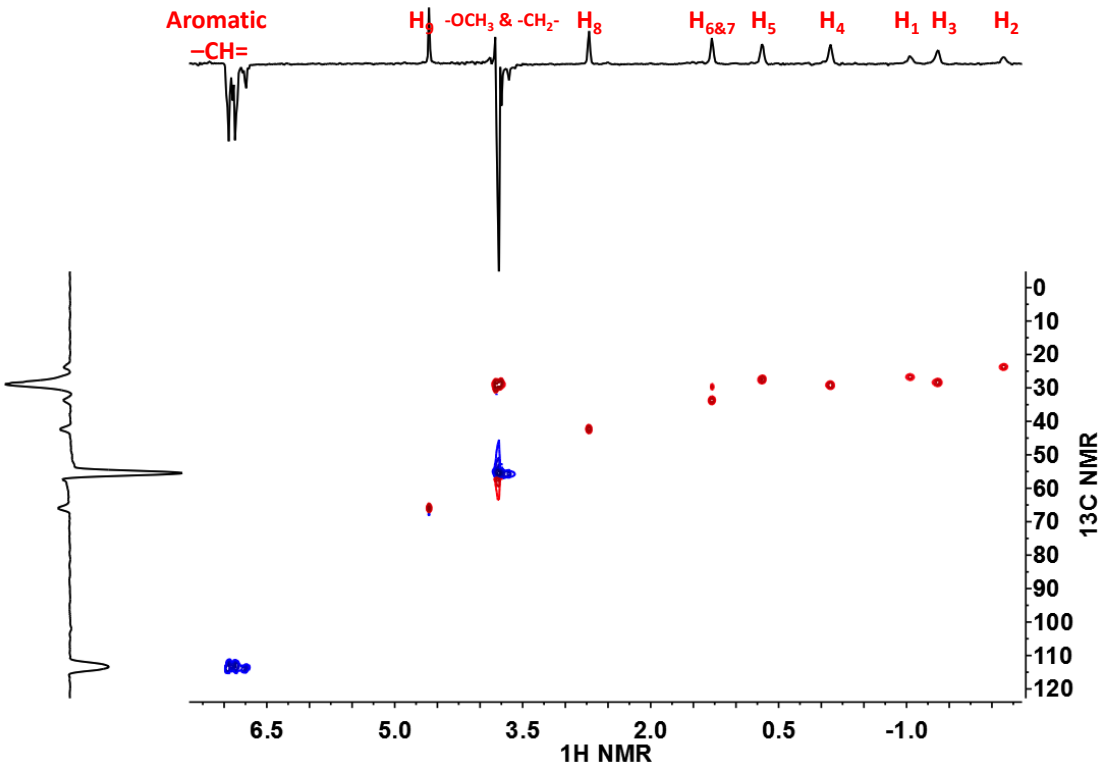


Figure S19. Full spectrum of HSQC to the **PR**. H_1-H_9 are in accordance with Table S1.

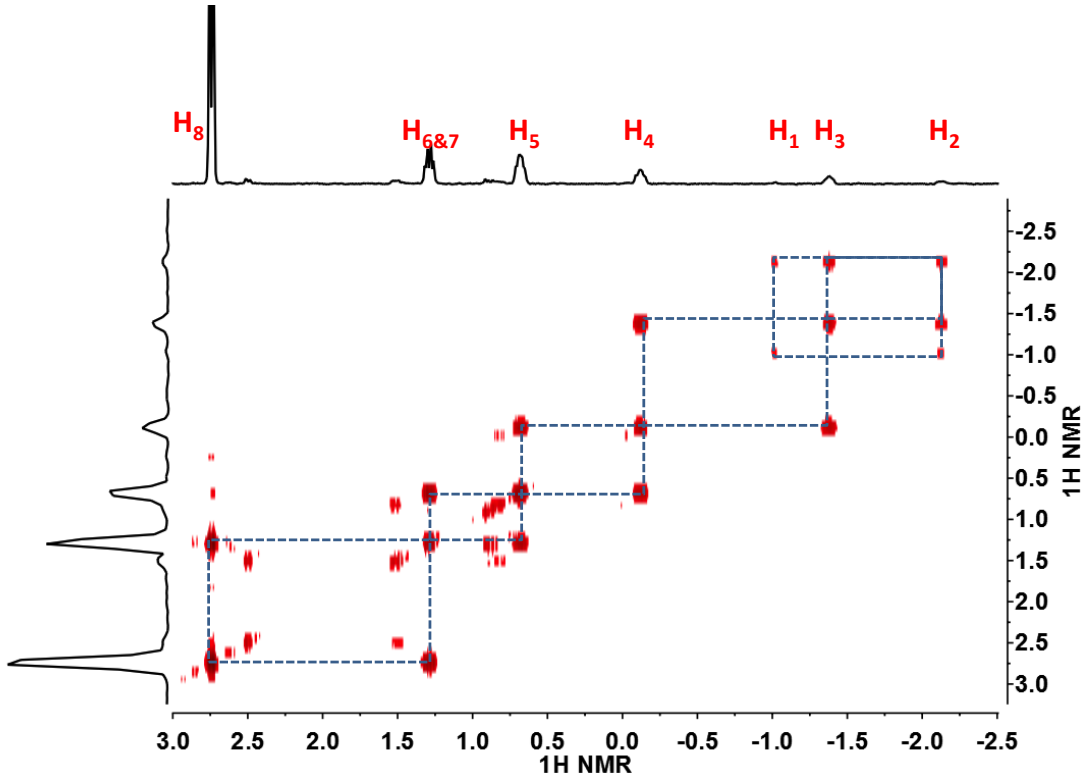
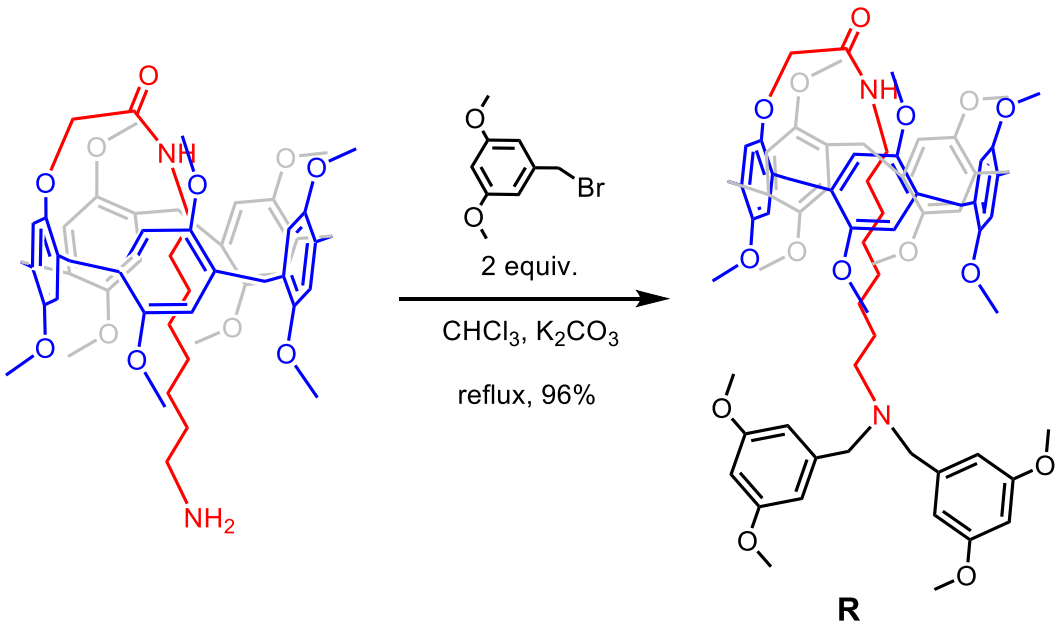


Figure S20. Partial spectrum of COSY to the **PR**. Correlation of all the hydrogens along the pending chain of **PR**, in which H_8 was known to assign other signals as shown in arrow above. H_1-H_9 are in accordance with Table S1.

7) Synthesis of R



R

To a 10.0 mL round-bottom flask, **PR** (276.3 mg, 0.3 mmol) and 1-(bromomethyl)-3,5-dimethoxybenzene (276.8 mg, 1.2 mmol) were dissolved in 6.0 mL $CHCl_3$. The mixture was refluxed for 24 hours, and then the solvent was removed on rotor-vap. The crude product was purified by column chromatography (SiO_2, DCM : MeOH = 40 : 1) to give a yellow viscous semi-solid (351.4 mg, 96 %). ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ 7.08 – 6.24 (m, 16H), 5.04 (s, 1H), 4.56 (s, 2H), 4.21 – 3.28 (m, 53H), 2.63 – 2.16 (m, 3H), 1.52 (s, 1H), 1.38 (dd, *J* = 13.6, 7.0 Hz, 2H), 0.68 (s, 2H), -0.12 (s, 2H), -1.38 (d, *J* = 69.7 Hz, 4H), -2.38 (s, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.55, 161.15, 151.17, 150.86, 150.68, 150.60, 150.46, 150.34, 147.43, 142.89, 129.58, 129.39, 128.71, 128.53, 128.26, 128.10, 127.39, 127.12, 114.18, 114.11, 113.83, 113.68, 113.51, 113.13, 113.03, 112.77, 106.98, 98.48, 66.18, 59.04, 55.84, 55.77, 55.65, 55.59, 55.50, 55.08, 38.34, 30.62, 30.09, 29.59, 29.15, 28.91, 28.54, 26.76, 23.96. HRESIMS: m/z calcd for $[M+H]^+$ (100.00 %) $C_{72}H_{89}N_2O_{15}^+$, 1221.6257; found 1221.6245; m/z calcd for $[M+2H]^{2+}$ (74.61 %) $C_{72}H_{90}N_2O_{15}^{2+}$, 1222.6330; found 1222.6330. MALDI-TOF-MS: found 1221.126. m.p. 80.7-82.2 ℃ (melting at the earliest stage); 98℃ (to form liquid completely).

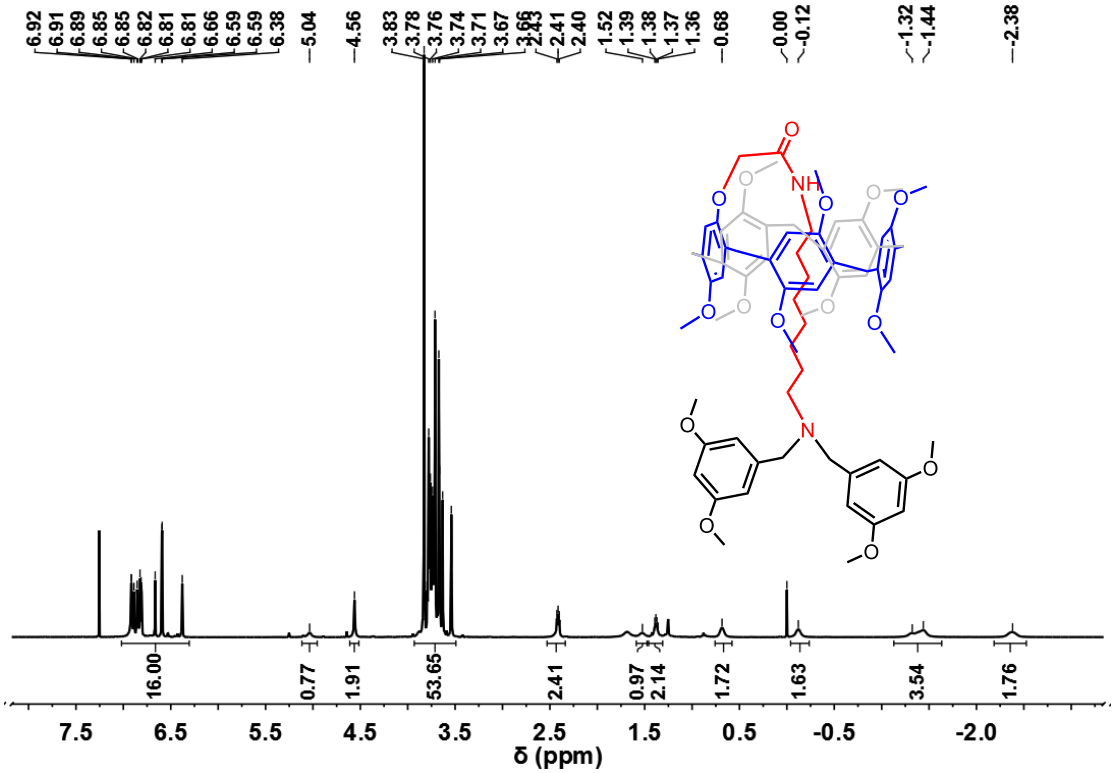


Figure S21. ^{1}H NMR spectrum of **R.**

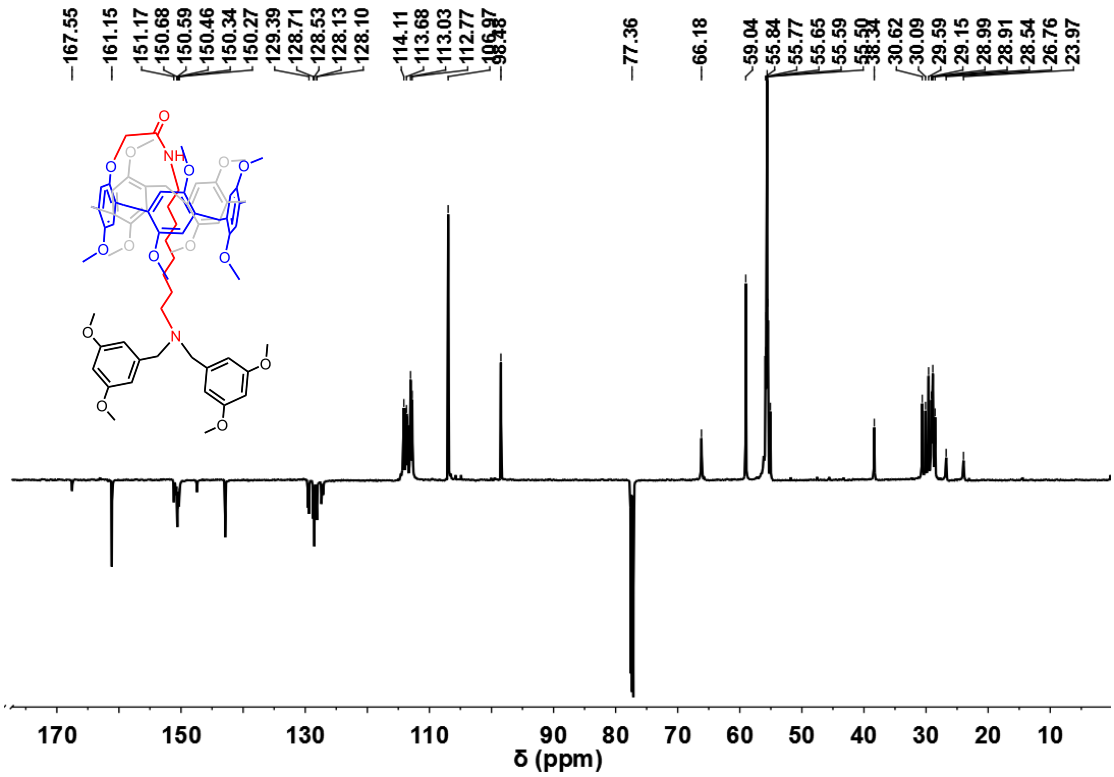


Figure S22. ^{13}C NMR spectrum of **R.**

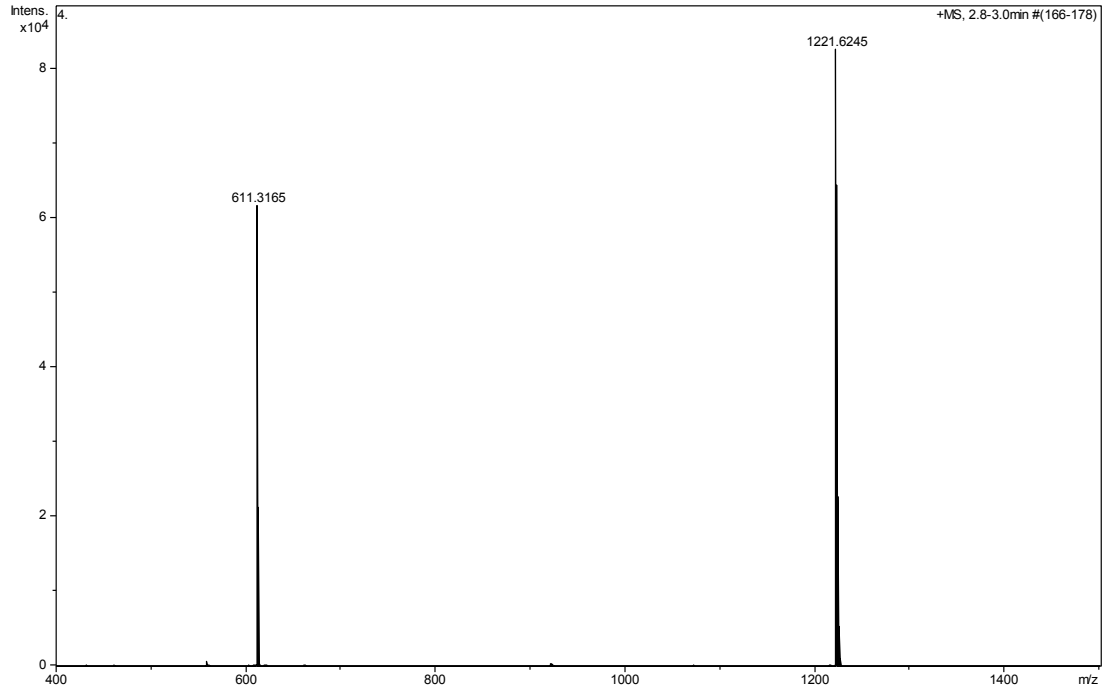


Figure S23. Mass spectrum of **R**. HRESIMS: m/z calcd for $[M+H]^+$ (100.00 %) $C_{72}H_{89}N_2O_{15}^+$, 1221.6257; found 1221.6245; m/z calcd for $[M+2H]^{2+}$ (74.61 %) $C_{72}H_{90}N_2O_{15}^{2+}$, 1222.6330; found 1222.6330.

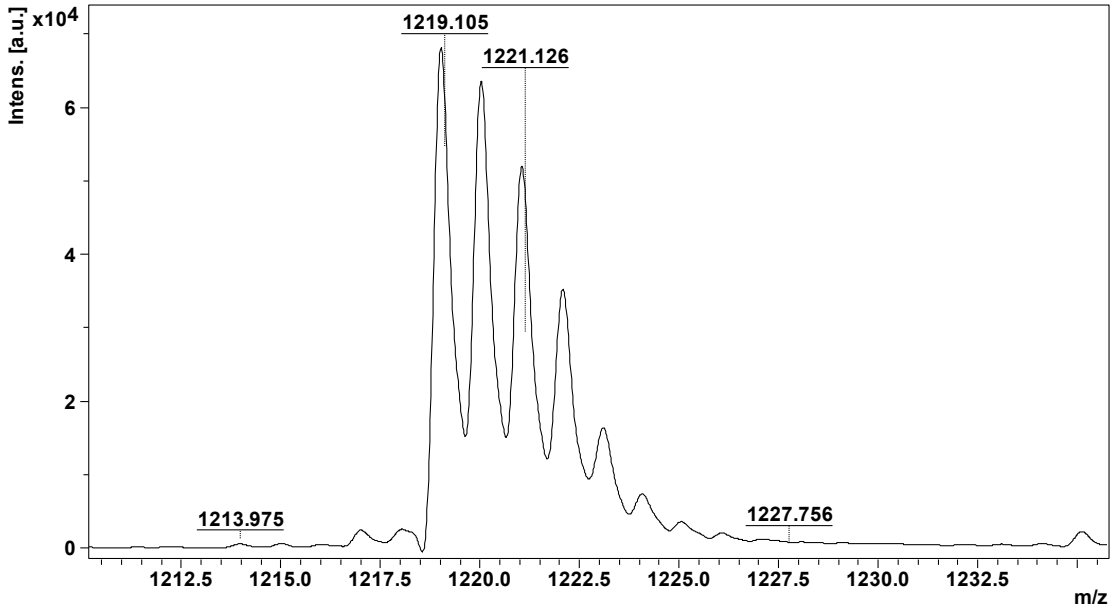


Figure S24. MALDI-TOF-MS of **R**

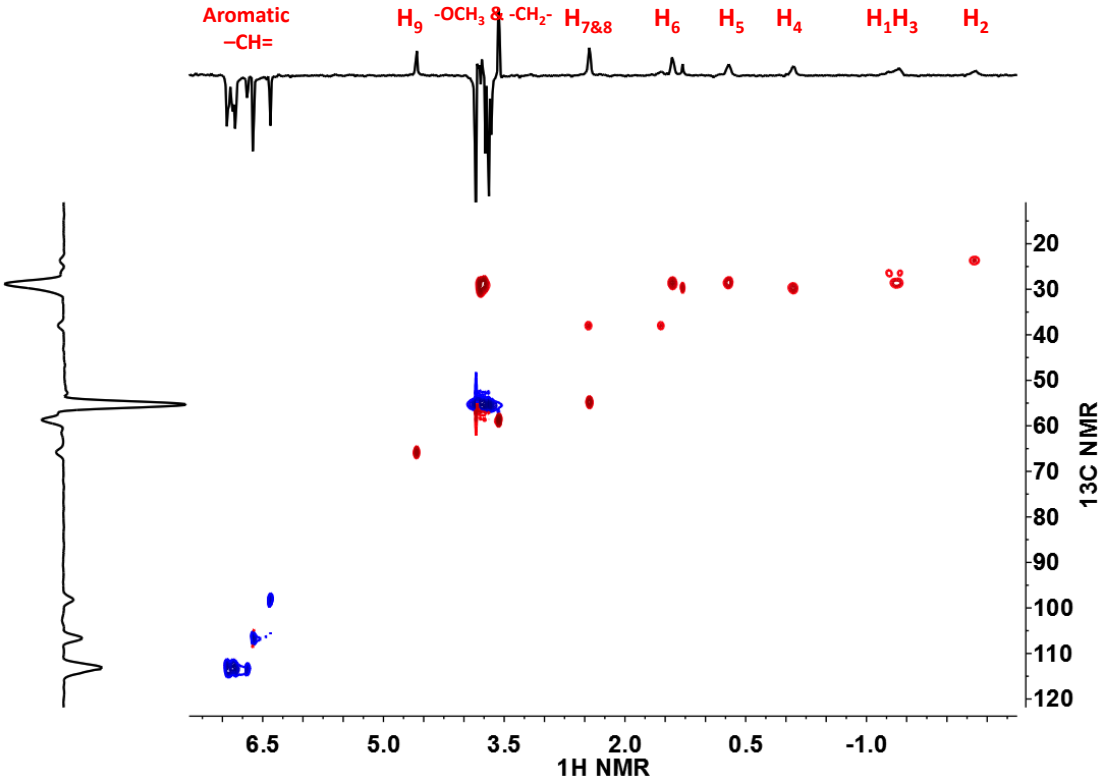


Figure S25. Full HSQC spectrum of the corresponding **R**. H_1-H_9 are in accordance with Table S1.

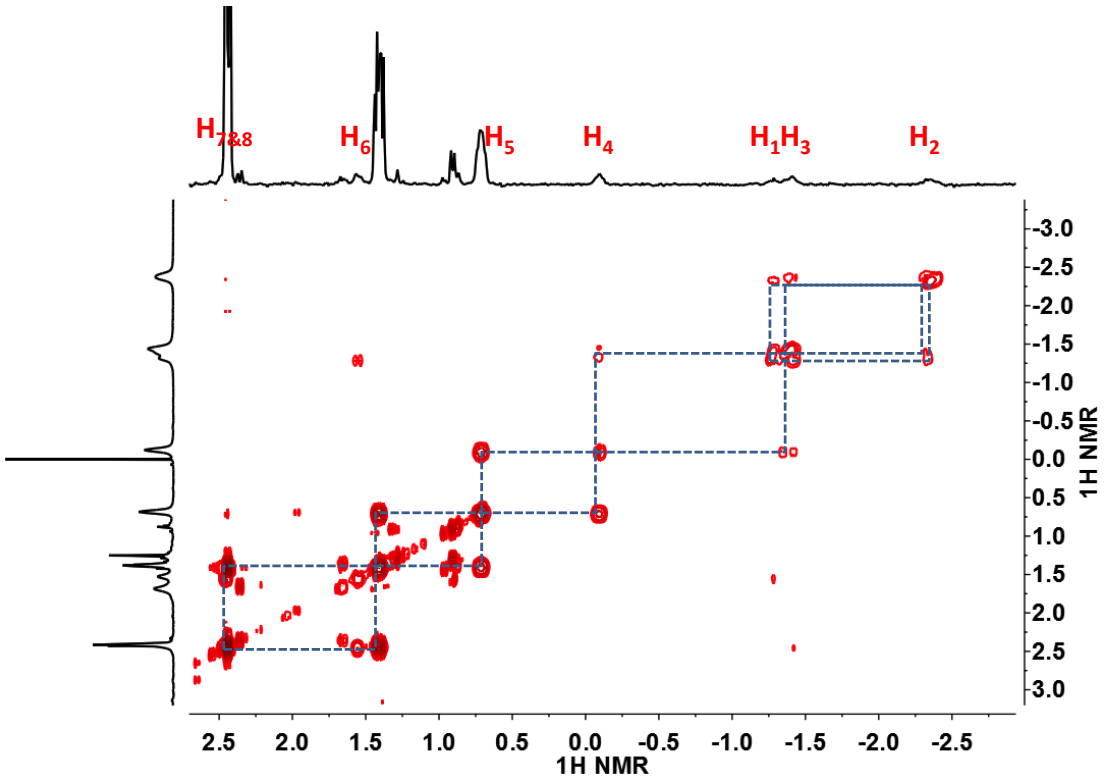
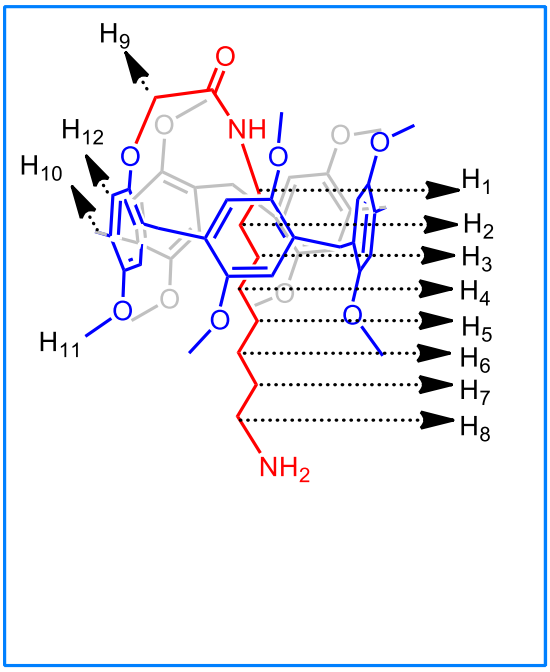
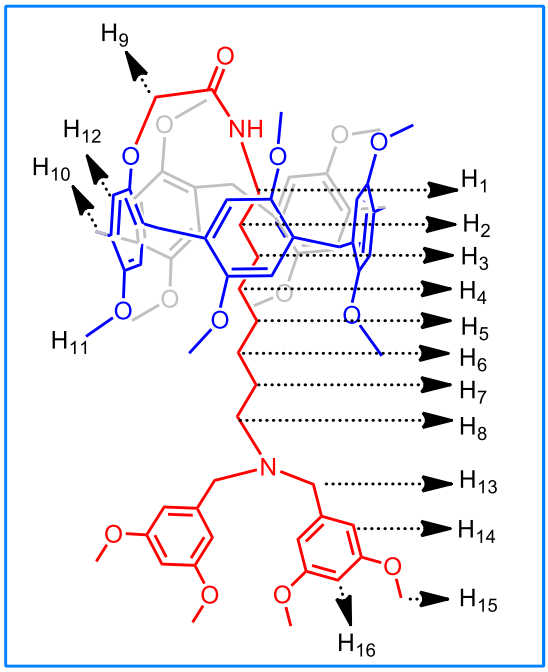


Figure S26. Partial COSY spectrum of the corresponding **R**. correlation of all the hydrogens along the pending chain of **R**, in which H_8 was known to assign other signals as shown in arrow above. H_1-H_9 are in accordance with Table S1.

Table S1. ^{1}H NMR and ^{13}C NMR data of the **PR** and **R** in $CDCl_3$ (δ values relative to $CHCl_3$ as the internal reference)

Compound	PR		R	
	^{1}H	^{13}C	^{1}H	^{13}C
H_1	-1.07	27.11	-1.32[a] -1.45[b]	26.76
H_2	-2.17	24.04	-2.38	23.96
H_3	-1.39	28.67	-1.41	28.92
H_4	-0.13	29.51	-0.12	30.09
H_5	0.67	27.78	0.68	28.87
H_6	1.25	30.01	1.38	28.92
H_7	1.25	34.03	2.42[a] 1.52[b]	38.34
H_8	2.70	42.69	2.40	55.19
H_9	4.57	66.37	4.56	66.12
H_{amide}	5.23		5.04	
H_{10}	3.69-3.81	27.65-31.93	3.68-3.78	27.91-31.97
H_{11}	3.61-3.80	51.61-57.73	3.59-3.78	54.14-56.95
H_{12}	6.69-6.95	111.69-115.61	6.64-6.91	112.07-114.93
H_{13}			3.50-3.54	57.97-60.24
H_{14}			6.59	107.14
H_{15}			3.80-3.85	54.24-56.95
H_{16}			6.36	98.65





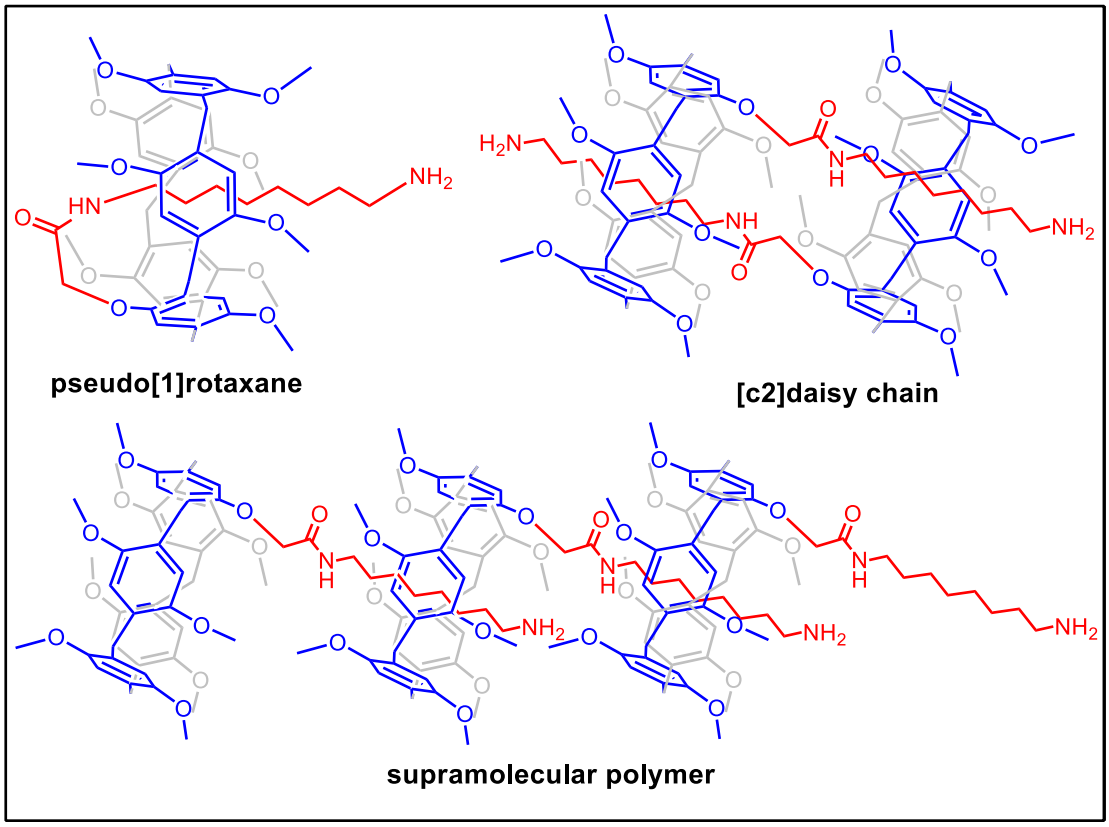


Figure S27. Description of the possible conformations or self-assembly for **PR** in $CHCl_3$.

3. Concentration independent NMR titration of PR

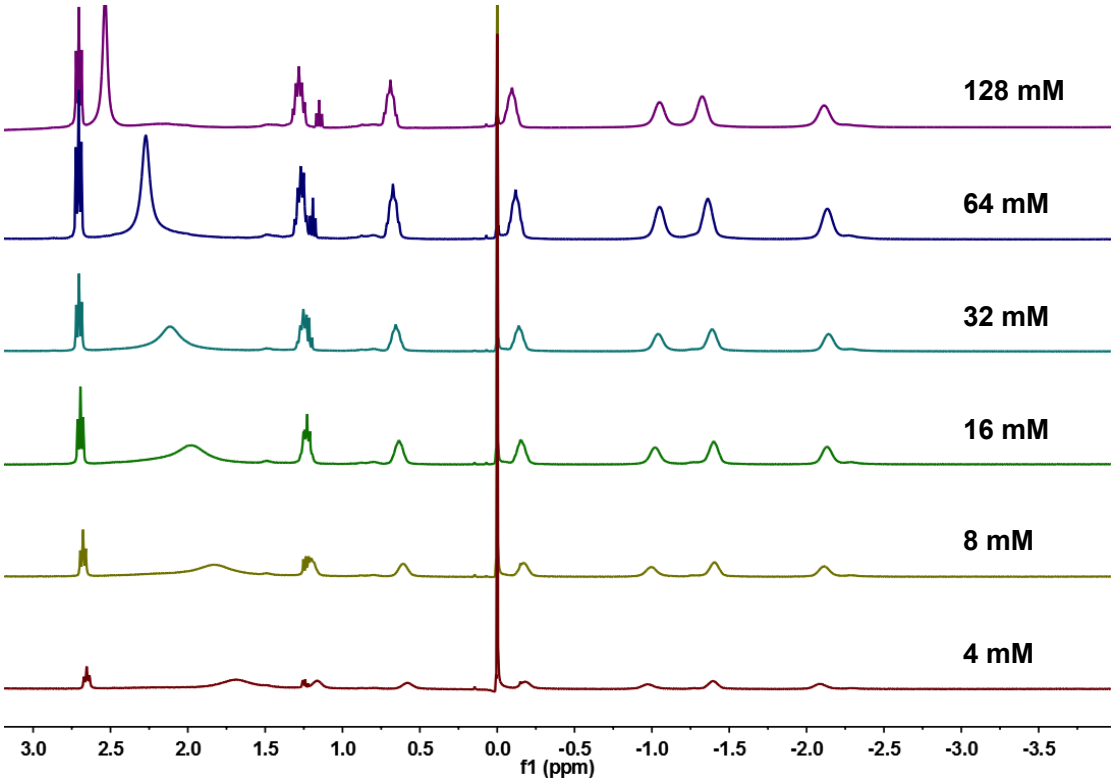


Figure S28. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum of **PR** with variable concentrations.

Table S2. ^{1}H NMR data of the representative –CH_2- of **PR** in $CDCl_3$ (δ values relative to TMS as the internal standard) with variable concentration.

[C]/mM	δ[ppm]						
	H_1	H_2	H_3	H_4	H_5	H_6&H_7	H_8
4	-0.97	-2.09	-1.40	-0.18	0.58	1.16	2.65
8	-1.00	-2.12	-1.41	-0.17	0.61	1.20	2.68
16	-1.02	-2.13	-1.40	-0.15	0.63	1.23	2.69
32	-1.04	-2.14	-1.39	-0.14	0.66	1.25	2.70
64	-1.05	-2.13	-1.36	-0.12	0.67	1.27	2.71
128	-1.05	-2.11	-1.33	-0.10	0.69	1.28	2.70

4. Knoevenagel reaction monitored by ^{1}H NMR.

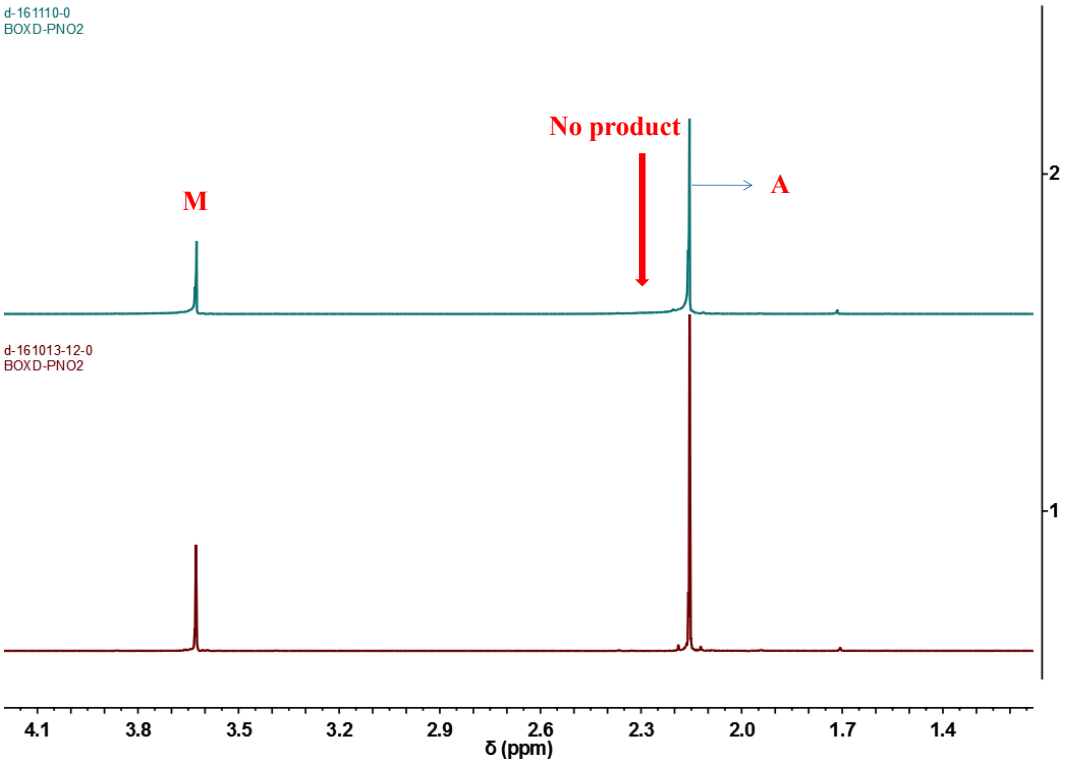


Figure S29. No condensation product formed in the absence of **R**.

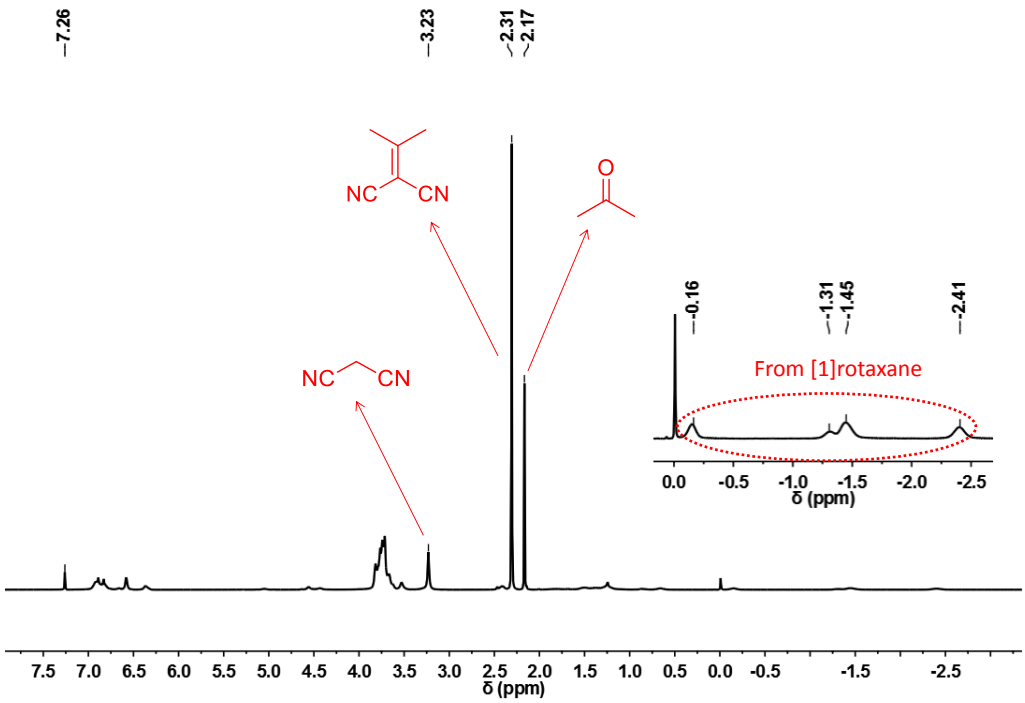


Figure S30. ^{1}H NMR spectrum of condensation mixture catalyzed by **R** (R.T., 10 mmol % **R**, 200 mM **A** and **M,** 600 hours). Labelled peaks are from the condensation product (2.31 ppm) which are coincided with the reported values[S4].

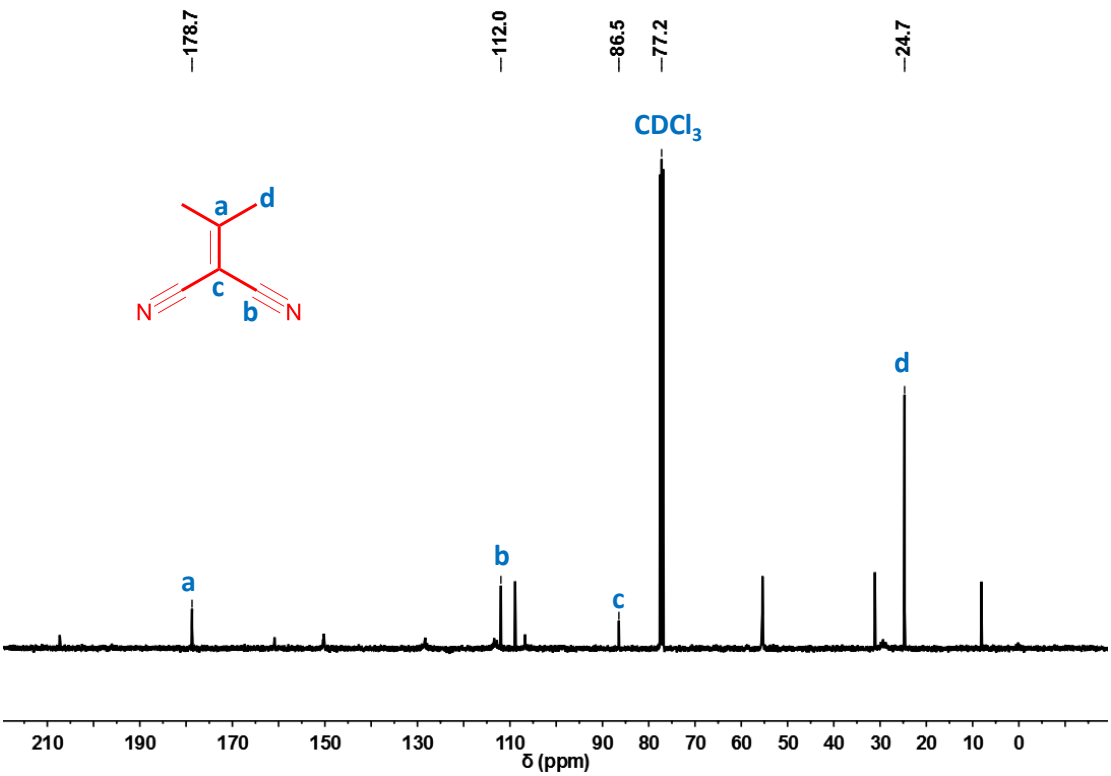


Figure S31. ^{13}C NMR spectrum of condensation mixture catalysed by **R** (R.T., 10 mmol % **R**, 200 mM **A** and **M,** 600 hours). Labeled peaks are from the condensation product and are in accordance with the reported values.[S4]

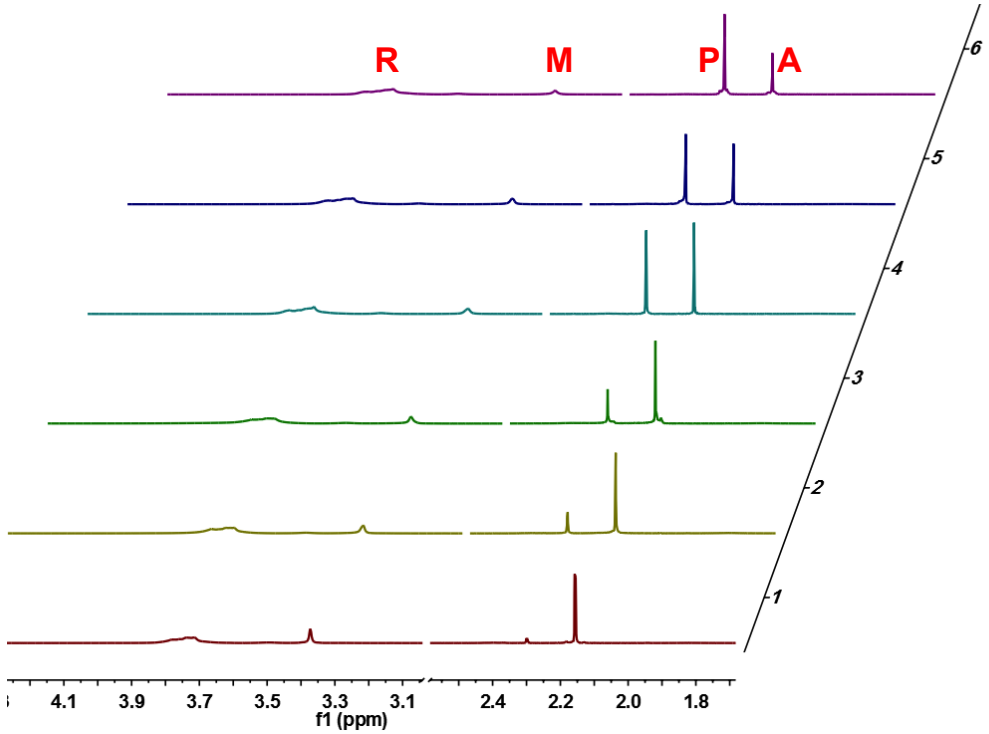
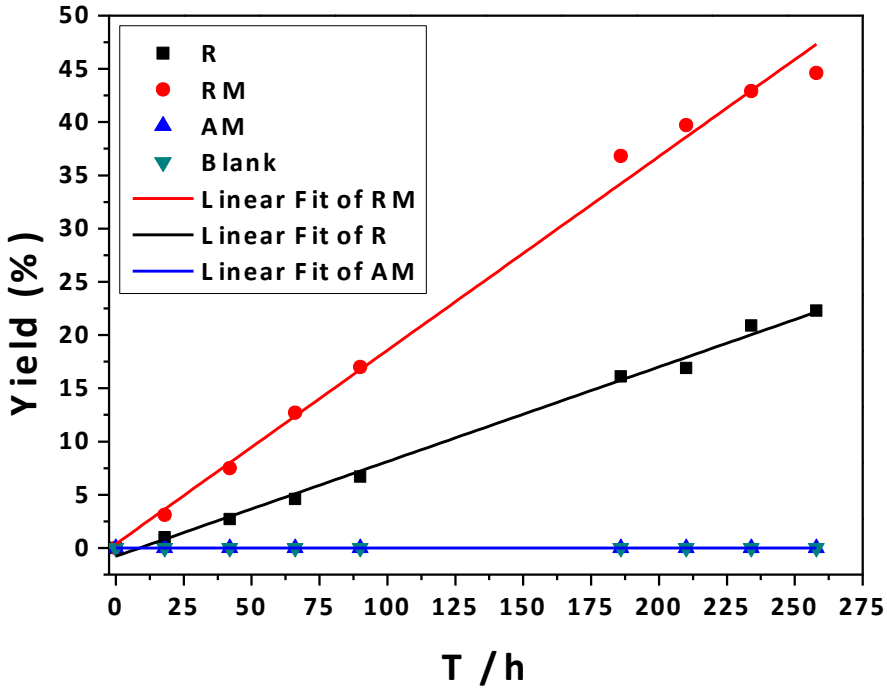


Figure S32. ^{1}H NMR monitoring the Knoevenagel reaction of malononitrile (**M**) and acetone (**A**) to produce product (**P**) catalysed by **R**, the selected spectrum from 1 to 6 recorded at 36 h, 120 h, 192 h, 360 h, 480 h and 600 h, respectively.



Equation	y = a + b*x		
Adj. R-Square	0.99299		
		Value	Standard Error
RM	Intercept	0.37056	0.83434
RM	Slope	0.18203	0.0054

Equation	y = a + b*		
Adj. R-Square	0.99437		
		Value	Standard Error
R	Intercept	-0.77671	0.3653
R	Slope	0.08894	0.00237

Equation	y = a + b*x		
Adj. R-Square	--		
		Value	Standard Error
AM	Intercept	0	0
AM	Slope	0	0

Figure S33. ^{1}H NMR monitoring the Knoevenagel reaction of malononitrile (**M**) and acetone (**A**) to produce product (**P**) catalysed by [1]rotaxane (**R**), monomer of [1]rotaxane (**RM**), amide monomer (**AM**) and no catalyst (blank).

5. The energy-minimized structure of PR and R.

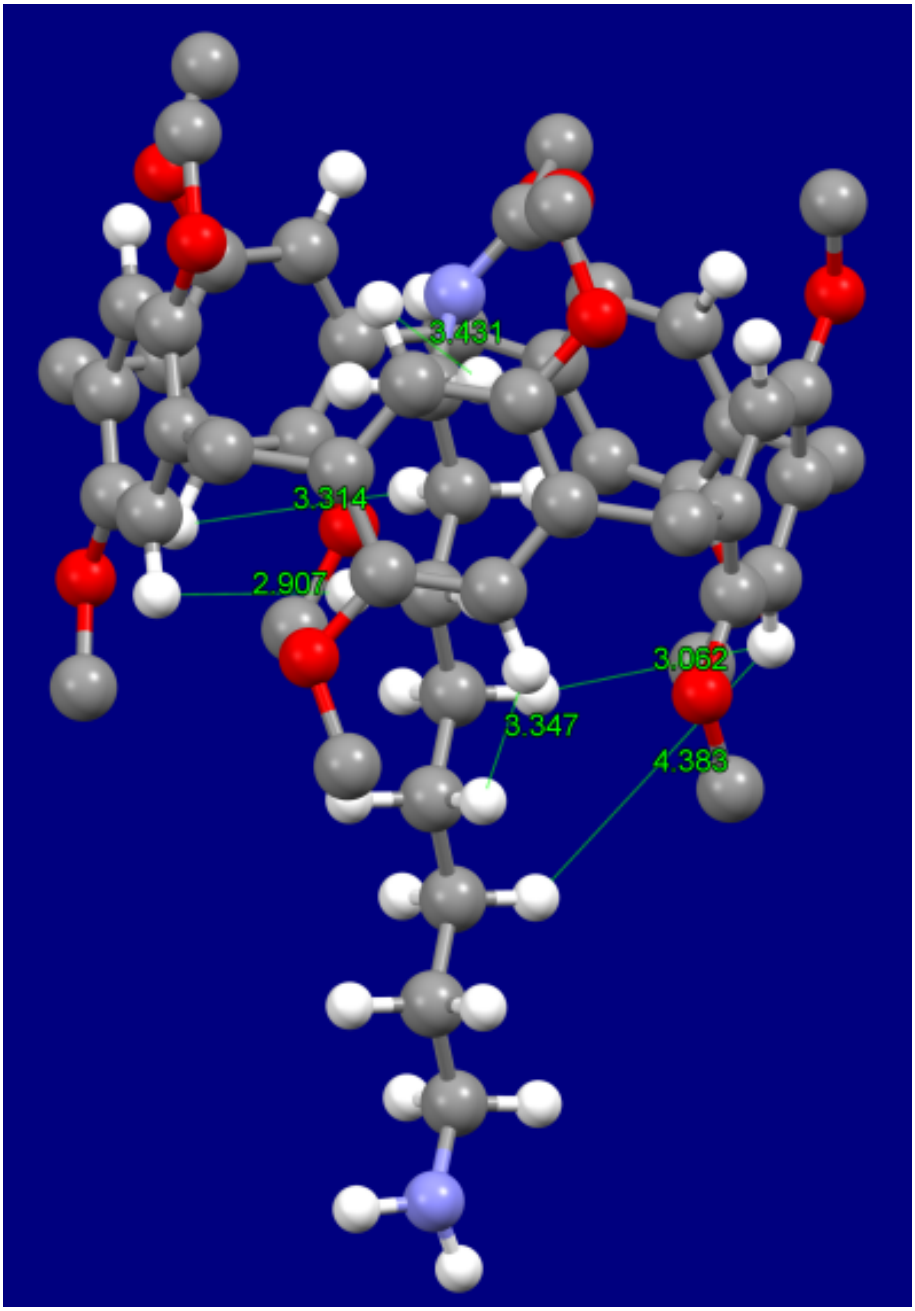


Figure S34. Hydrogens on pending chain of **PR** are close to hydrogens on pillar[5]arene (ArH) with the smallest distances H_1-ArH 3.431 **Å**, H_2-ArH 3.314 **Å**, H_3-ArH 2.907 **Å**, H_4-ArH 3.062 **Å**, H_5-ArH 3.347 **Å**, H_6-ArH 4.383 **Å**. H_1-H_6 are in accordance with Table S1.

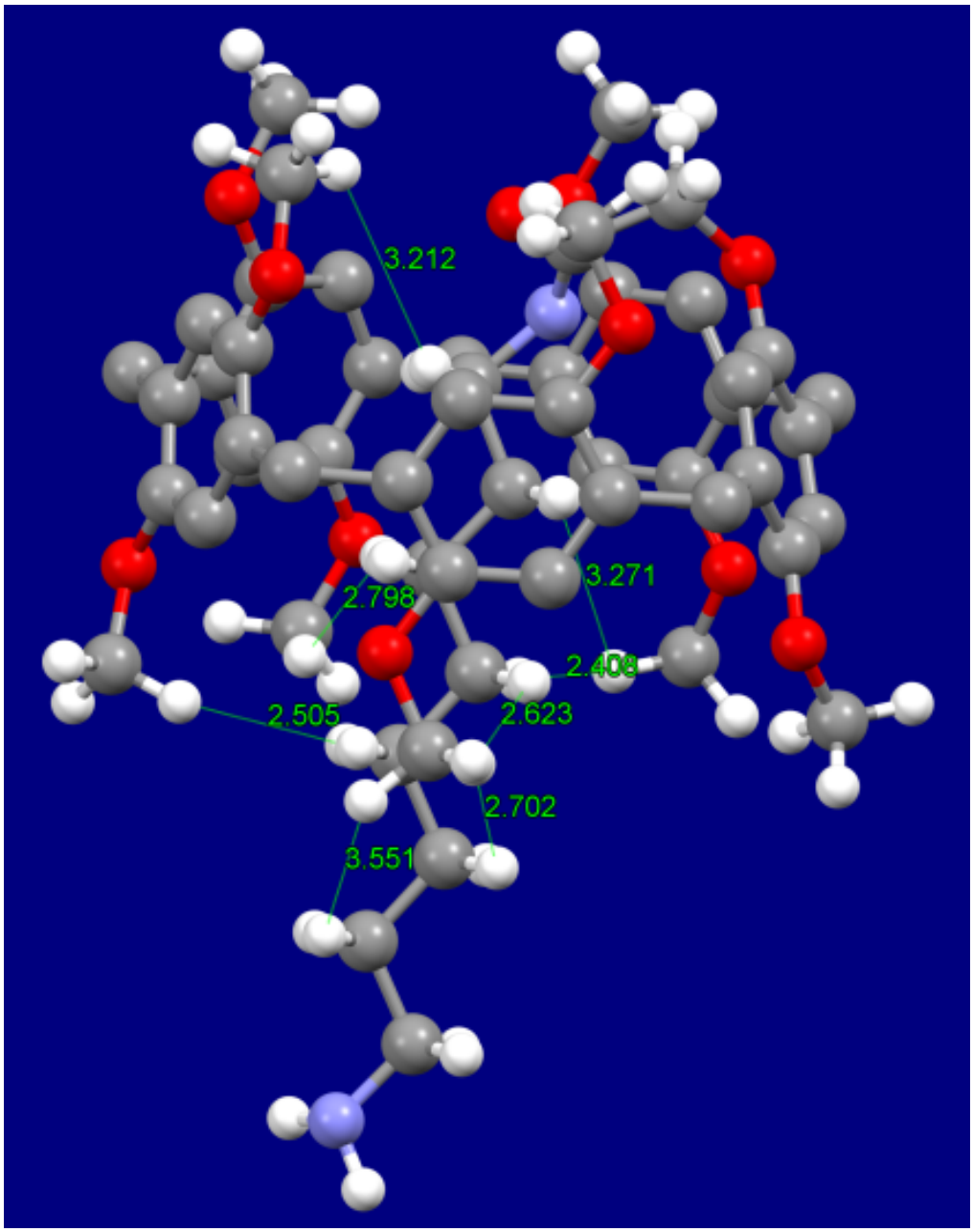


Figure S35. Hydrogens on pending chain of **PR** are close to hydrogens on pillar[5]arene (-OCH_3) with the smallest distances H_1-OCH_3 3.212 **Å**, H_2-OCH_3 3.271 **Å**, H_3-OCH_3 2.798 **Å**, H_4-OCH_3 2.406 **Å**, H_5-OCH_3 2.505 **Å**, H_6-OCH_3 2.702 **Å**, H_7-OCH_3 3.551 **Å**. H_1-H_7 are in accordance with Table S1.

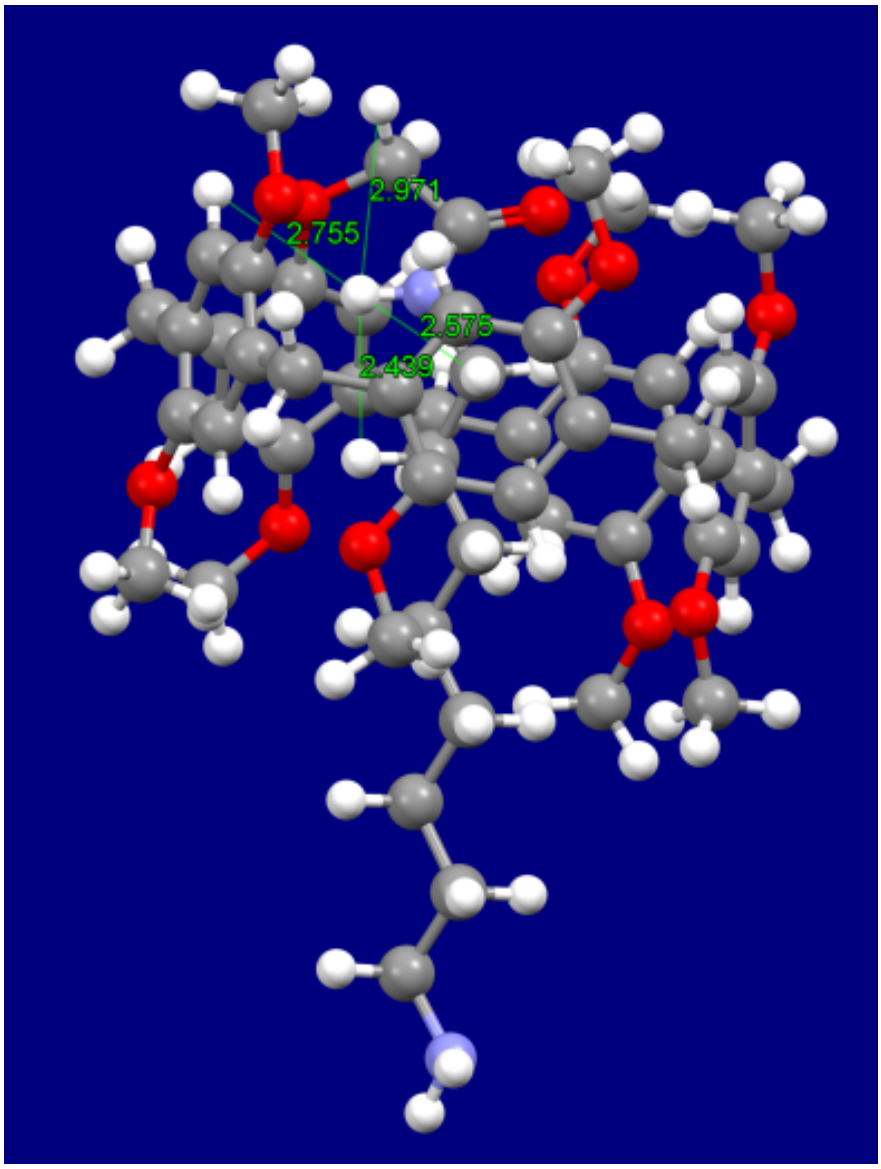


Figure S36. Hydrogen of –NH- of **PR** are close to hydrogens on pillar[5]arene (ArH and $–OCH_2CO-$) with the smallest distances NH-ArH 2.439 **Å**, NH-OCH_2CO 2.971 **Å**.

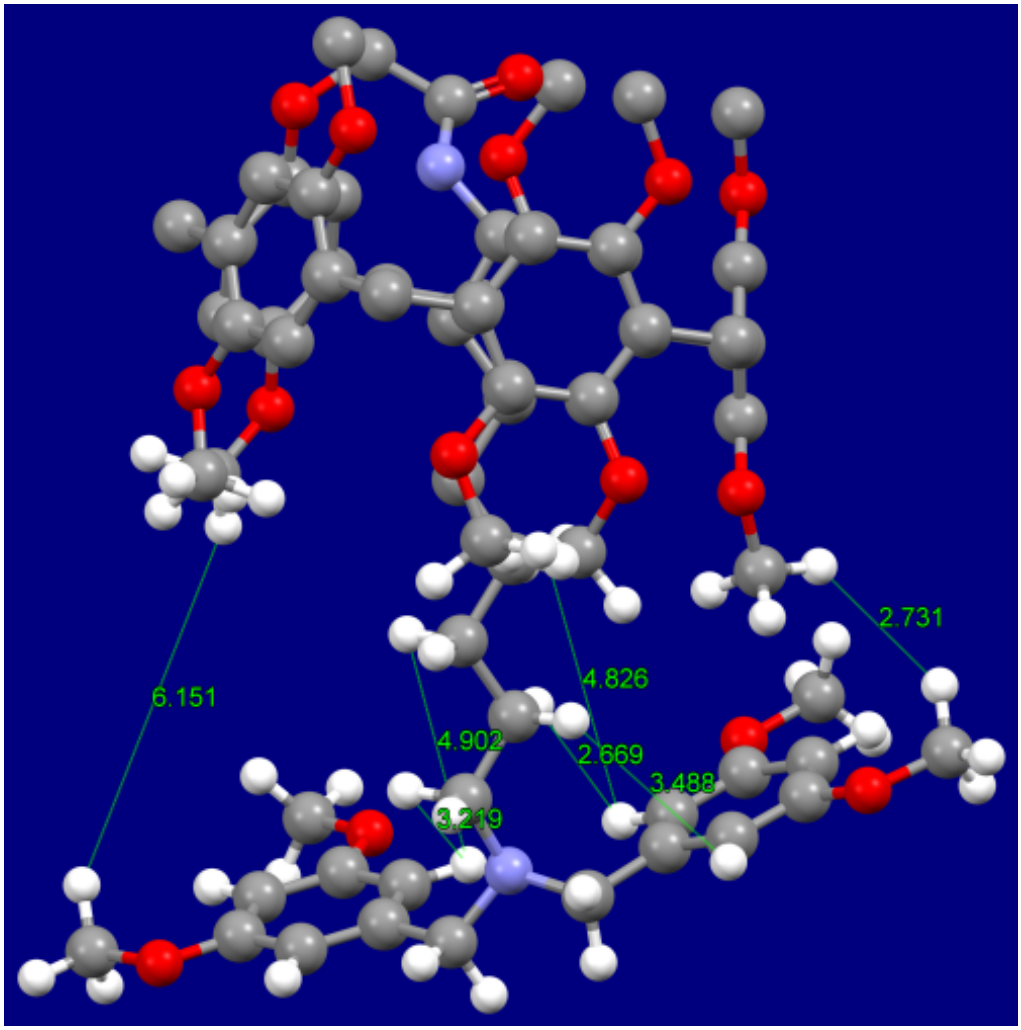


Figure S37. Hydrogens on stopper (H* from ArH and $H^{@}$ from $–OCH_3$) of **R** are close to hydrogens on pillar[5]arene ($-OCH_3$) and pending chain from H_5 to H_8 with the smallest distances H_5-H* 4.826 **Å**, H_6-H* 4.902 **Å**, H_7-H* 2.669 **Å**, H_8-H* 3.219 **Å**, $H^{@}$-OCH_3 2.731 **Å**. H_5-H_8 are in accordance with Table S1.

6. Appendix

PR xyz coordinates:

C	-4.20260700	-0.40609000	-2.34384200
C	-4.06933100	0.98885600	-2.35897700
C	-2.98433700	1.61420800	-2.99500100
C	-2.06115400	0.79503800	-3.67410700
C	-2.18725400	-0.60080900	-3.64732400
C	-3.24144300	-1.22589800	-2.96500900
H	-4.78992700	1.61714200	-1.85228000
H	-1.45218500	-1.23200300	-4.13081700
C	-2.80795200	3.12793500	-2.93383500
H	-2.49063600	3.49090800	-3.91594800
H	-3.78009700	3.57975900	-2.71159800
C	-1.78835300	3.59881700	-1.89752900
C	-0.50546800	4.01738900	-2.28479000
C	-2.08519000	3.60901600	-0.52380600
C	0.45736100	4.39650300	-1.33831800
H	-0.26364600	3.99624600	-3.33929000
C	-1.14220200	4.02306200	0.41886700
C	0.15130700	4.40416700	0.03711300
H	-1.37167200	4.02469200	1.47679800
C	1.19505600	4.75538600	1.09651700
H	0.78684000	5.52807200	1.75625400
C	1.61015900	3.55536000	1.94166700
C	0.88448800	3.18299700	3.08956200
C	2.70887500	2.76276600	1.57705300
C	1.21502700	2.02385200	3.80071700
C	3.05176700	1.61144000	2.30055900
H	3.28215700	3.05640800	0.70549200
C	2.28833600	1.20791500	3.41309300
H	0.62804000	1.71150600	4.65326700
H	2.07429300	5.16975400	0.59997000
C	2.60186600	-0.07769600	4.17414100
H	2.33450600	0.06528900	5.22539600
C	1.86323800	-1.29961900	3.63653400
C	0.52868500	-1.56520900	4.00493100
C	2.48287600	-2.18006500	2.73845600
C	-0.16907000	-2.63995300	3.43951900
C	1.78987100	-3.26679300	2.18710200
H	3.50868200	-1.97917300	2.45598400
C	0.44154000	-3.50056900	2.51415600

H	-1.20554400	-2.82246700	3.69335400
H	3.67736600	-0.26626400	4.12258500
C	-0.34434400	-4.63826300	1.87003100
H	-1.03869600	-5.05161900	2.60603100
C	-1.13391100	-4.20431700	0.63936400
C	-2.47499500	-3.78644700	0.74062800
C	-0.53204400	-4.17875500	-0.62752000
C	-3.17422000	-3.34089000	-0.38852100
C	-1.22890600	-3.72624000	-1.75620700
H	0.50030300	-4.49672000	-0.70254400
C	-2.56324900	-3.29011500	-1.65082700
H	-4.19884500	-3.00077700	-0.30965200
C	-3.31598500	-2.74487100	-2.86089600
H	-4.36506100	-3.04464500	-2.79276400
H	-2.89539400	-3.18587400	-3.76769100
O	1.76140500	4.77279700	-1.68447100
O	-3.36703200	3.13477200	-0.15550400
O	-1.03111300	1.45957700	-4.34782100
O	-5.26184200	-1.06743500	-1.70832400
O	-0.65977300	-3.66944300	-3.03704500
O	-3.04436400	-3.84237600	2.02043600
O	2.37267700	-4.16400300	1.27792300
O	-0.02660700	-0.70981600	4.96239300
O	4.14818700	0.80041000	1.96882600
O	-0.16647000	4.03339600	3.45862100
C	3.81190800	-4.10495100	1.06751600
H	4.04362100	-4.95479900	0.42606600
H	4.10471900	-3.17643300	0.56676600
H	4.35233000	-4.19646100	2.01620600
C	5.14576900	1.32986500	1.04951600
H	5.95871000	0.60430800	1.05674800
H	4.74651500	1.42118100	0.03422100
H	5.51240400	2.30532000	1.38807500
C	2.13478300	4.79345700	-3.09010800
H	3.17433600	5.11905600	-3.10536600
H	2.05238500	3.79685400	-3.53769900
H	1.51735400	5.50112200	-3.65438200
C	-0.12619500	0.68260500	-5.18247400
H	0.52615900	1.41524400	-5.65628800
H	0.47327100	-0.01035300	-4.58278200
H	-0.67669500	0.12442900	-5.94770800
C	0.67492900	-4.21496700	-3.23203400
H	0.87223300	-4.11600300	-4.29891100
H	1.42235200	-3.64968100	-2.66481800

H	0.71715900	-5.27077400	-2.94255500
C	-6.32882600	-0.27414400	-1.11629500
H	-7.05206100	-0.99892100	-0.74459900
H	-5.95531000	0.33392800	-0.28533800
H	-6.80182500	0.37334200	-1.86252600
C	-4.43010100	-3.43036000	2.18577600
H	-4.64554000	-3.56853700	3.24462500
H	-4.56486300	-2.37766500	1.91436400
H	-5.10291000	-4.05345000	1.58628200
C	-1.44248500	-0.84619100	5.28699300
H	-1.62932200	-0.09428100	6.05340900
H	-2.05795500	-0.63709600	4.40783000
H	-1.66166000	-1.84125400	5.68913800
C	-0.97209100	3.68491300	4.62547300
H	-1.67869500	4.50765200	4.73501200
H	-1.50874100	2.74858700	4.45013500
H	-0.35045600	3.61333600	5.52459400
C	-3.55543600	2.62833000	1.19935200
H	-4.60286700	2.31834600	1.23110500
H	-3.40483600	3.40831400	1.95045400
C	-2.63440200	1.45269600	1.54492900
O	-2.36639700	1.20880000	2.75372900
N	-2.16975500	0.74922400	0.49142600
H	-2.51147100	1.01188400	-0.42656200
C	-1.02348000	-0.17305300	0.52599400
H	-1.35504400	-1.18282300	0.26359800
H	-0.65232800	-0.19912900	1.55306900
C	0.06176400	0.31245700	-0.45417000
H	0.37679000	1.32081600	-0.15800900
H	-0.38502100	0.40327500	-1.45377500
C	1.29138000	-0.60590100	-0.53994100
H	1.78432400	-0.65445800	0.43974700
C	2.30229000	-0.12284800	-1.59707700
H	1.81246000	-0.09622600	-2.58286700
H	2.59042700	0.91555700	-1.37195300
C	3.56852400	-0.99284700	-1.68658900
H	3.28261700	-2.03166000	-1.91414300
H	4.05839200	-1.01622200	-0.70154100
C	4.57459200	-0.50203200	-2.74345100
H	4.08223500	-0.47783100	-3.72778100
H	4.85812400	0.53757400	-2.51641500
C	5.84483300	-1.36631200	-2.82794300
H	5.56352500	-2.40428500	-3.06641000
H	6.34748500	-1.39518700	-1.85161700

C	6.84517300	-0.86453000	-3.87847400
H	6.32670700	-0.78207200	-4.85331700
H	7.17100900	0.14943200	-3.61307100
N	8.04040900	-1.72244500	-3.92330100
H	7.83601400	-2.67694800	-4.20816200
H	8.79476400	-1.33995500	-4.48578400
H	0.97256900	-1.62976500	-0.78174700
H	0.35397000	-5.42815100	1.58219500

R xyz coordinates:

C	5.32536200	-2.02800000	-2.91155100
C	5.22163500	-3.08658700	-1.99801900
C	4.02040200	-3.79461800	-1.83084700
C	2.93258400	-3.44654800	-2.65516600
C	3.03418400	-2.38298300	-3.56265500
C	4.21773900	-1.64049100	-3.68931900
H	6.06650300	-3.37192700	-1.38433700
H	2.18574200	-2.08791700	-4.16720600
C	3.89700600	-4.88644800	-0.77258700
H	3.30970800	-5.71430100	-1.18041100
H	4.89735600	-5.26708200	-0.54620200
C	3.23343300	-4.41667500	0.52112900
C	1.86672900	-4.64317200	0.74868500
C	3.94895800	-3.71620700	1.50817700
C	1.22674800	-4.15880200	1.89740600
H	1.30838600	-5.16726400	-0.01532100
C	3.32216200	-3.26451300	2.67309600
C	1.94907600	-3.45741200	2.88324600
H	3.87048600	-2.71545200	3.42800200
C	1.26043700	-2.87814400	4.11770100
H	1.84403700	-3.14081800	5.00561600
C	1.10806400	-1.36155500	4.06278700
C	2.13858400	-0.51300100	4.51226800
C	-0.05009500	-0.76597100	3.54103600
C	2.03505600	0.87542500	4.36962700
C	-0.16916900	0.62740700	3.43111400
H	-0.85352100	-1.41318100	3.20895500
C	0.89276500	1.47058300	3.81254000
H	2.84939900	1.52401200	4.66180200
H	0.27439800	-3.33594100	4.21570200
C	0.82033300	2.98318900	3.62253400
H	1.41556500	3.46196900	4.40613200

C	1.32418600	3.44942800	2.25981400
C	2.70265000	3.59113000	2.00080700
C	0.43085200	3.72112900	1.21494500
C	3.15912800	3.93387900	0.72252500
C	0.88645200	4.08119500	-0.06122400
H	-0.62797700	3.60846600	1.41102200
C	2.26397400	4.17228800	-0.33288800
H	4.21865700	4.00525400	0.51208300
H	-0.21721900	3.30644100	3.74194200
C	2.78010300	4.49593100	-1.73248300
H	3.64598000	5.15816500	-1.64703800
C	3.18620900	3.25918400	-2.52777900
C	4.50625400	2.76925300	-2.49465200
C	2.24376000	2.55131300	-3.28846600
C	4.85422700	1.59857000	-3.18019800
C	2.58966000	1.37537900	-3.96893600
H	1.22795800	2.92638200	-3.31268700
C	3.90419400	0.87418700	-3.91612500
H	5.86340400	1.20960300	-3.13929400
C	4.28617000	-0.42921400	-4.61259000
H	5.30378500	-0.33770600	-5.00207500
H	3.61268800	-0.58822600	-5.45806700
O	-0.14264800	-4.32787600	2.13735000
O	5.31561000	-3.46606900	1.22931400
O	1.77437000	-4.21522100	-2.50040400
O	6.50257300	-1.29313800	-3.10185600
O	1.67191300	0.62826100	-4.72197500
O	5.42391400	3.51329400	-1.73842400
O	0.01787600	4.34684000	-1.13272500
O	3.55510400	3.37988900	3.09045200
O	-1.32333400	1.25883400	2.94084300
O	3.24402900	-1.14271400	5.09888400
C	-1.39857800	4.52930500	-0.84630000
H	-1.84265300	4.87716400	-1.77845100
H	-1.86965800	3.58888600	-0.54434400
H	-1.54491000	5.28025500	-0.06185400
C	-2.56497900	0.49476900	2.88899200
H	-3.34744900	1.22500100	2.68084000
H	-2.53963800	-0.25457700	2.09094500
H	-2.75896700	0.00208300	3.84822300
C	-0.94763600	-5.01777800	1.14127600
H	-1.96093500	-5.01656700	1.54133700
H	-0.92731500	-4.48980900	0.18144200
H	-0.60692000	-6.04944900	0.99990800

C	0.63574600	-3.94876600	-3.36788300
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H	0.23526300	-2.94382600	-3.19852400
H	0.90715900	-4.06459100	-4.42285000
C	0.33906100	1.17312000	-4.93675200
H	-0.15393200	0.46926400	-5.60648400
H	-0.21891600	1.24040000	-3.99687400
H	0.38804400	2.16167500	-5.40634600
C	7.69533800	-1.67544200	-2.35975500
H	8.47619900	-0.99906200	-2.70511800
H	7.54660400	-1.54887200	-1.28206400
H	7.98057500	-2.71104200	-2.57428300
C	6.81238100	3.07853900	-1.70308600
H	7.32685300	3.81322300	-1.08485100
H	6.90503300	2.08473200	-1.25188200
H	7.24898700	3.06765900	-2.70784500
C	4.99736600	3.40761900	2.87815300
H	5.43023500	3.28987000	3.87127400
H	5.31318500	2.57472500	2.24318100
H	5.31719900	4.36343700	2.44966500
C	4.32391100	-0.31437700	5.62767300
H	5.00784900	-1.01608000	6.10524000
H	4.83541700	0.20780000	4.81558000
H	3.94485700	0.39427600	6.37204000
C	5.99357500	-2.39359400	1.95008900
H	7.02018200	-2.42180700	1.57703400
H	6.01320200	-2.57513500	3.02815800
C	5.36406500	-1.01709900	1.70949800
O	5.52345000	-0.09378400	2.55409400
N	4.64817800	-0.90150500	0.57218500
H	4.64417100	-1.69644000	-0.05752200
C	3.61989800	0.12448600	0.33240500
H	3.98211100	0.87837800	-0.37475000
H	3.42826400	0.62687100	1.28482100
C	2.35506800	-0.56650600	-0.20586300
H	2.09156400	-1.38568700	0.47600200
H	2.59168200	-1.02454000	-1.17530300
C	1.14226900	0.35877600	-0.36978000
H	0.84086800	0.74297900	0.61310700
C	-0.05064400	-0.36529800	-1.02227700
H	0.21498100	-0.64508000	-2.05373600
H	-0.24230200	-1.30715800	-0.48459700
C	-1.33777100	0.47533800	-1.02776600
H	-1.15233500	1.42481500	-1.55279800

H	-1.58288900	0.74467200	0.01020600
C	-2.54630900	-0.23582100	-1.66470400
H	-2.37727600	-0.35573200	-2.74599300
H	-2.62878000	-1.25244900	-1.24993400
C	-3.86449900	0.51835500	-1.41340000
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C	-5.07163300	-0.15264600	-2.08125600
H	-4.96023900	-0.09864300	-3.18452100
H	-5.07324900	-1.21525900	-1.81417500
N	-6.38697000	0.39594700	-1.67037100
H	1.41370400	1.23109100	-0.97723400
C	-6.60642200	1.80387500	-2.05985900
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C	-6.05630400	2.84126600	-1.08838200
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C	-5.52165300	3.57314500	1.15702400
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C	-5.21370200	5.08180600	-0.69284300
H	-5.69804800	4.32058200	-2.63850200
C	-5.13178800	4.83656200	0.68612900
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C	-7.34986000	-1.83583800	0.08938400
C	-7.86231000	-4.21608800	-1.28146500
H	-7.91205900	-3.02060300	-3.06302300
C	-7.43040000	-3.04935300	0.78062400
H	-7.14179400	-0.92467200	0.63529600
C	-7.68907700	-4.25514800	0.10886100
H	-7.74962700	-5.18835200	0.64954000
O	-8.11757500	-5.34593500	-2.05552700
O	-7.23988900	-2.96937900	2.15870500
O	-4.84837000	6.29271100	-1.27963100
O	-5.45580300	3.20506300	2.50174400
C	-7.31855200	-4.18618800	2.95521200
H	-6.55028200	-4.90679800	2.65428800
H	-7.14181000	-3.86755400	3.98158700
H	-8.30898200	-4.64756000	2.87637300

C	-8.21857300	-6.64254700	-1.39979400
H	-8.42355900	-7.35230100	-2.20004800
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C	-5.01029100	4.18745800	3.48222800
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C	-4.43703100	7.39772400	-0.42389000
H	-3.52223400	7.15495500	0.12743600
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H	-5.23137600	7.66841000	0.27997400
H	1.99864900	5.02918600	-2.27928200

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