Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

2D and 3D Metal-Organic Frameworks Constructed with A Mechanically Rigidified [3]Rotaxane Ligand

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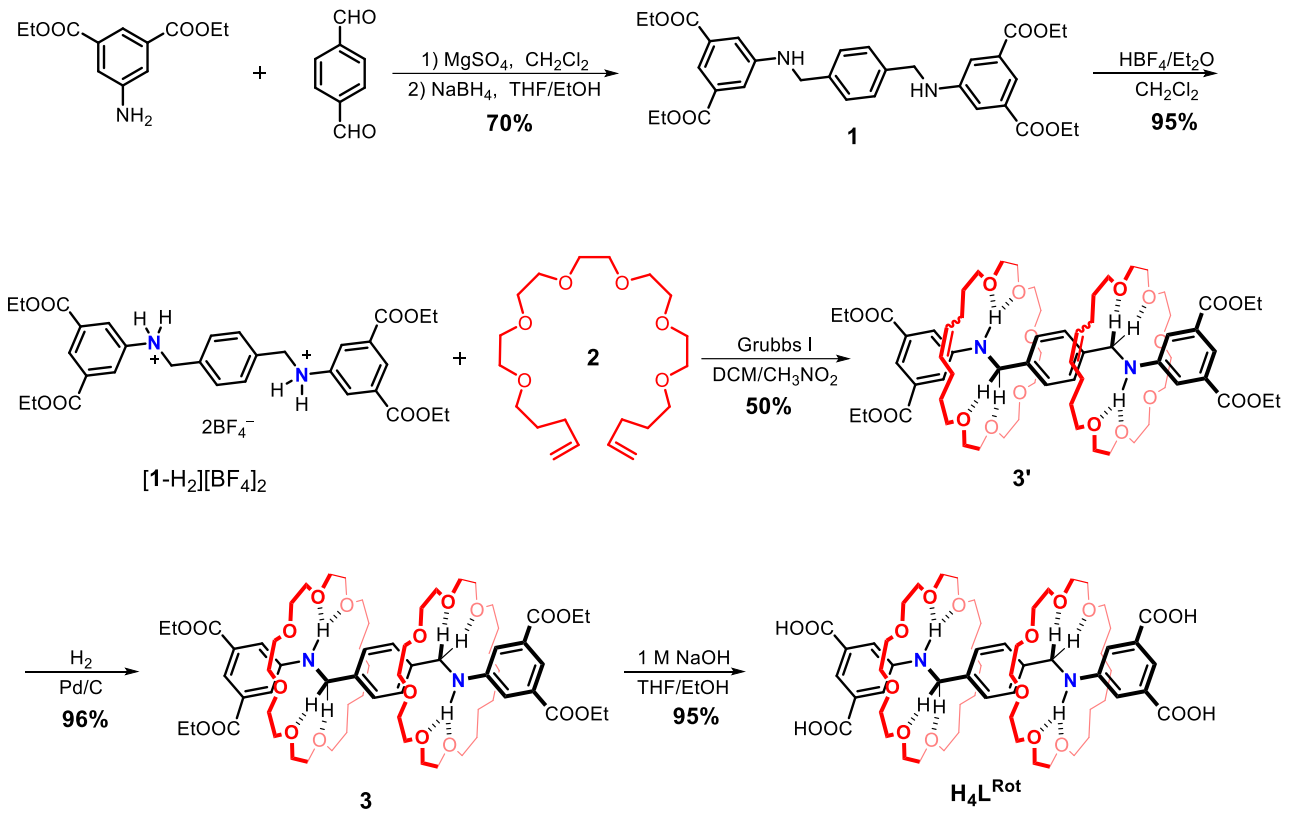
Table of Contents

1. Materials and General Methods

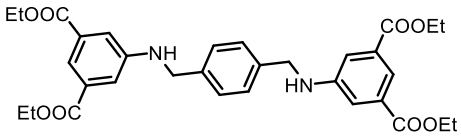
Diethyl-5-amino-isophthalate[S1] and pentaethyleneglycol-dipent-4-enyl ether **3**[S2] were synthesized according to literature. All reagents were purchased from commercial suppliers and used without further purification unless stated otherwise. Tetrahydrofuran (THF), dichloromethane (DCM) and *N*,*N*-Dimethylformamide (DMF) were degassed and dried under nitrogen by passing them through a Vigor VSGS-5 Solvent Purification System. Flash column chromatography was performed over silica gel (200-300 mesh). NMR spectra were recorded on a JEOL 400YH instrument. NMR spectra were internally referenced to tetramethylsilane (^{1}H) or alternatively, to the residual proton solvent signal (^{13}C). All ^{13}C NMR spectra were recorded with complete proton decoupling. High-resolution mass spectra were measured on a Bruker AutoFlex Times TOF. The single crystal X-ray diffraction (SCXRD) data was collected on an Agilent Sapphire3 Gemini Ultra single crystal diffractometer using using a CuKα (λ = 1.54178 Å). Powder X-ray diffraction (PXRD) was tested on Rigaku smartlab with CuKα (λ = 1.540598 Å). Thermogravimetric analyses (TGA) were carried out in a nitrogen stream using a DTA-60 Simultaneous DTG-TG Apparatus (Shimadzu) with a heating rate of 5 °C min^{-1}. Infrared spectroscopy was performed on a Bruker Vertex70 Hyperion 3000 FT-IR spectrometer.

2. Synthesis of the [3]rotaxane 3 and ligand H_4L^{Rot}

Scheme S1. Synthesis of [3]rotaxane **3** and ligand $\mathbf{H_4L^{Rot}}$.



Compound 1[S3]

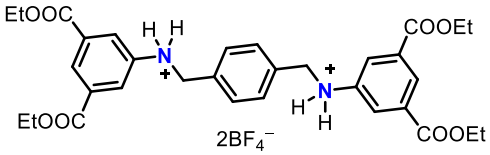


Diethyl-5-amino-isophthalate [S1] (8.29 g, 35.0 mmol) and terephthalaldehyde (2.24 g, 16.7 mmol) were stirred for 24 h in DCM with excess $MgSO_4$ at room temperature. The solution was filtered and evaporated to yield a pale yellow solid. The solid was dissolved in a 3:1 mixture of THF/EtOH (200 mL) and 5 equivalents (3.16 g) of $NaBH_4$ slowly added. The mixture was stirred at room temperature for 12 h. And then the reaction was quenched by the addition of an aqueous solution of HCl (1 M). The organic solvent was subsequently removed and extraction was performed using EtOAc and H_2O. The organic layers were combined and dried over $MgSO_4$ and the solvent removed. The crude product was purified by column chromatography on silica gel with (petroleum ether/

ethyl acetate =2/1) to yield a white solid; yield (6.73 g, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (t, J = 1.6 Hz, 2H), 7.47 (d, J = 1.6 Hz, 4H), 7.36 (s, 4H), 4.69 (s, 4H), 4.40 (s, 2H), 4.36 (q, J = 7.2 Hz, 8H), 1.39 (t, J = 7.2 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 148.2, 140.4, 137.9, 131.8, 127.8, 127.5, 119.6, 117.6, 65.0, 61.3, 48.0, 14.4. HRMS (m/z): $[M+H]^+$ calcd. for $C_{32}H_{37}N_2O_8$, 577.2544, found: 577.2543.

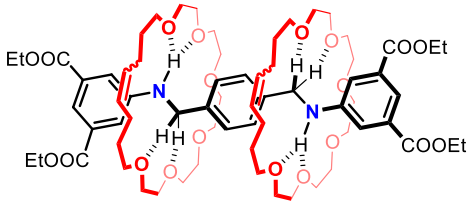
Compound [**1**-H_2][BF_4]$_2$ [S3]



Compound **1** (576 mg, 1.00 mmol) was just completely dissolved in DCM (30 mL) and 2.2 equivalents of HBF_4/Et_2O added with stirring. A white solid precipitated and was filtered under vacuum and then washed 3 times with Et_2O; yield (714 mg, 95%). This compound was employed directly in the next step without further purification.

^{1}H NMR (400 MHz, CD_3CN) δ 8.54 (t, J = 1.6 Hz, 2H), 8.11 (d, J = 1.6 Hz, 4H), 7.47 (s, 4H), 4.68 (s, 4H), 4.39 (q, J = 7.2 Hz, 8H), 1.38 (t, J = 7.2 Hz, 12H). ^{13}C NMR (400 MHz, CD_3CN) δ 164.2, 136.3, 133.2, 132.1, 131.1, 129.7, 127.0, 117.4, 62.1, 54.9, 13.5. HRMS (m/z): $[M - HBF_4 - BF_4^-]^+$ calcd. for $C_{32}H_{37}N_2O_8$, 577.2544, found: 577.2542.

Compound 3′[S3]

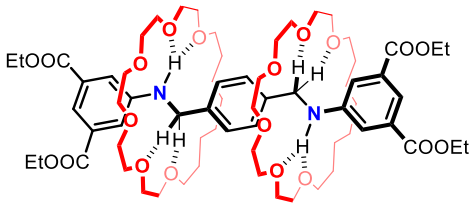


Pentaethyleneglycol-dipent-4-enyl ether [S2] (970 mg 2.58mmol) and [**2**-H_2][BF_4]$_2$ (650 mg, 0.86 mmol) was dissolved in $MeNO_2$ (4 mL) which were added to degassed DCM (40 mL) under an N_2 atmosphere. To this solution was added Grubbs I catalyst (71 mg, 10 mol%) and the mixture heated at 42 °C for 12 h after which another 10% catalyst was added and the reaction continued for a further 24 h. The solvent was removed via a rotary evaporator and the residue washed with isopropyl ether. The remaining material was dissolved in EtOAc (20 mL) and saturated aqueous

solution of $NaHCO_3$ (20 mL), then stirring for another 1 h. Then extracted with EtOAc and the organic layers were combined and dried with anhydrous Na_2SO_4, filtered, and concentrated in vacuum. The crude product was purified by column chromatography on silica gel with (petroleum ether/ ethyl acetate =4/1) as eluent to give the product **3′** (545 mg, 50% yield) as an off white solid. A [2]rotaxane with *E* and *Z* mixture was isolated as the main by-product (ca. 20% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.85 (m, 2H), 7.79–7.72 and 7.68–7.66 (m, 4H), 7.71 and 7.69 (s, 4H), 5.87–5.83 (m, 2H), 5.28 (t, J = 3.6 Hz) and 5.14 (t, J = 4.8 Hz, 4H), 4.67 (t, J = 4.4 Hz) and 4.51 (t, J = 5.2 Hz, 4H), 4.39–4.33 (m, 8H), 3.62–3.17 (m, 48H), 2.16–1.87 (m, 8H), 1.62–1.43 (m, 8H), 1.40–1.36 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.22, 167.16, 150.40, 150.28, 138.62, 138.35, 138.03, 137.76, 131.02, 130.87, 130.21, 129.68, 129.31, 129.26, 128.86, 128.74, 118.36, 117.84, 117.02, 72.00, 71.04, 70.84, 70.70, 70.61, 70.56, 70.37, 70.32, 60.81, 60.75, 47.46, 47.10, 30.61, 29.31, 28.72, 25.16, 14.54. HRMS (m/z): $[M+H]^+$ calcd. for $C_{68}H_{105}N_2O_{20}$, 1269.7255, found: 1269.7261.

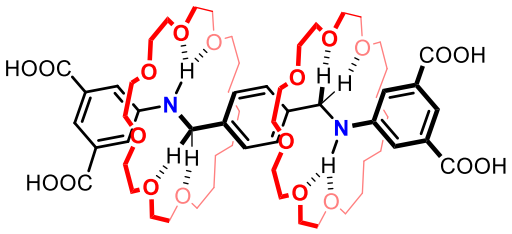
Compound 3



Pd/C 10 wt% (100 mg 0.048 mmol) was added to compound **3′** (305 mg 0.24 mmol) dissolved in EtOAc (40 mL). A slight vacuum was applied to the reaction mixture until boiling of the solvent was observed. The reaction vessel was flushed with H_2, introduced via a balloon, and the mixture stirred vigorously for 1 h under ambient conditions. The mixture was filtered through Celite and evaporated on a rotary evaporator to yield a white crystalline solid; yield (293 mg, 96%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (t, J = 1.6 Hz, 2H), 7.73 (d, J = 1.6 Hz, 4H), 7.71 (s, 4H), 5.81 (t, J = 4.8 Hz, 2H), 4.60 (d, J = 4.4 Hz, 4H), 4.37 (q, J = 7.2 Hz, 8H), 3.62–3.23 (m, 48H), 1.50–1.40 (m, 8H), 1.39 (t, J = 7.2 Hz, 12H), 1.35–1.21 (m, 8H), 1.13–1.06 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.21, 150.28, 138.22, 130.91, 128.99, 118.17, 117.04, 71.58, 71.08, 70.67, 70.65, 70.61, 70.46, 60.77, 47.17, 29.96, 29.03, 25.79, 14.54. HRMS (m/z): $[M+H]^+$ calcd. for $C_{68}H_{109}N_2O_{20}$, 1273.7568, found: 1273.7575.

[3]rotaxane linker H_4L^{Rot}



[3]rotaxane **3** (420 mg 0.33 mmol) was dissolved in a 1:1 mixture of EtOH/THF (15 mL) to which 1M NaOH was added (5 mL). The solution was refluxed over-night. After which the non-aqueous solvent was removed with a rotary evaporator. To the remaining solution distilled water was added (5 mL) and the solution was acidified dropwise with 1M HCl to pH=4 to yield a white precipitate. The solid was slowly filtered and washed with pH=4 water and then Et_2O several times and left to dry; yield (363 mg, 95%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 12.67 (s, 4H), 7.70–7.64 (m, 6H), 7.61 (s, 4H), 5.85 (t, J = 4.8 Hz, 2H), 4.54 (d, J = 4.4 Hz, 4H), 3.58–3.15 (m, 48H), 1.43–1.23 (m, 8H), 1.26–1.16 (m, 8H), 1.08–0.99 (m, 8H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.2, 150.4, 138.1, 131.7, 128.7, 117.7, 117.1, 71.1, 70.8, 70.6, 70.5, 70.3, 47.0, 29.9, 29.3, 25.7. HRMS (m/z): $[M+H]^+$ calcd. for $C_{60}H_{93}N_2O_{20}$, 1161.6316, found: 1161.6325.

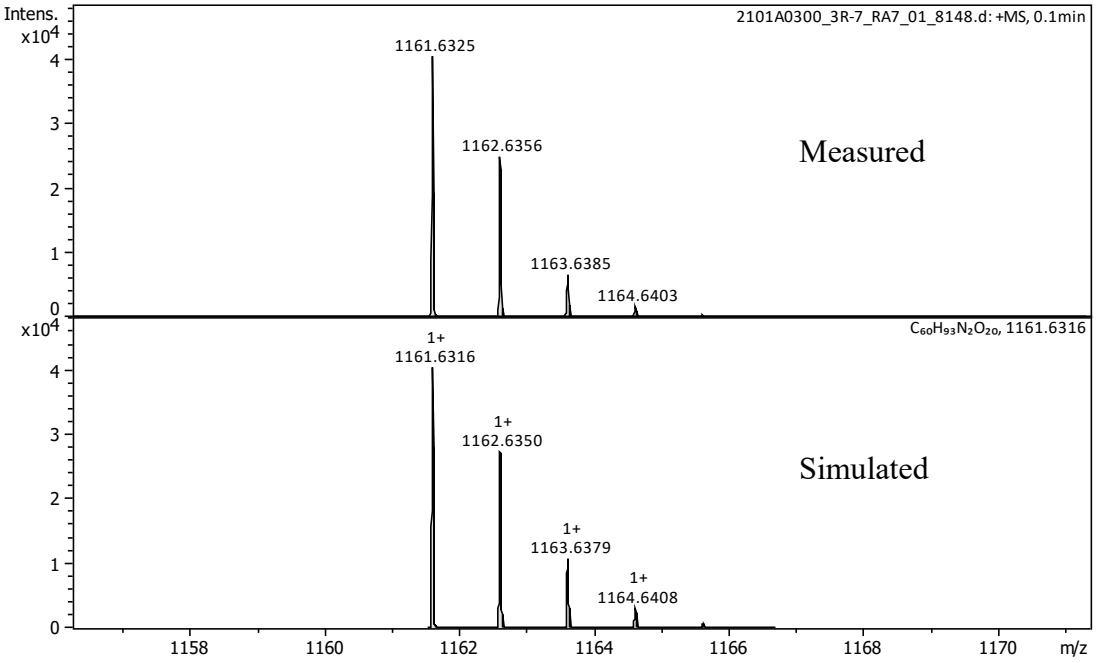


Figure S1. HRMS of the [3]rotaxane linker $\mathbf{L_{Rot}}$. Insets display the measured (top) and the simulated (bottom) isotope pattern.

3. Preparation of MOF-1 and MOF-2

MOF-1: **H_4L^{Rot}** (10 mg, 0.0086 mmol) and $Zn(NO_3)_2$•$6H_2O$ (10.18 mg, 0.0344 mmol) were added to a solution of H_2O/pyridine/DMF (1:1:8, 2.0 mL). Upon sonication, a clear solution was obtained. The mixture was then placed in a programmable oven and heated at a constant rate of 5 °C·min^{-1} to 85 °C and kept at that temperature for 5 days to obtain pale yellow crystals as **MOF-1**. Yield: 7.0 mg, 51% (based on ligand).

MOF-2: **H_4L^{Rot}** (10 mg, 0.0086 mmol) and $Zn(AcO)_2$ (6.31 mg, 0.0344 mmol)was dissolved in DMF (2 mL), to which 2 drops of 1.4 M HNO_3 were added. After sonication, the sample was placed in the programmable oven together with the above sample. After heating for 5 days, pale yellow **MOF-2** crystals were achieved. Yield: 5.3 mg, 45% (based on ligand).

4. Single crystal X-ray crystallography

Crystals were frozen in paratone oil inside a cryoloop under a cold stream of N_2. Reflection data were collected either on a Rigaku SuperNova, Dual, AtlasS2 diffractometer using monochromatized Cu Kα radiation or on a BRUKER D8 VENTURE PHOTON III diffractometer using Ga Kα radiation. Diffraction data and unit-cell parameters were consistent with assigned space groups. Lorentzian polarization corrections and empirical absorption corrections, based on redundant data at varying effective azimuthal angles, were applied to the data sets. The structures were solved using OLEX^2 crystallography software.[S5,S6] When practical, non-hydrogen atoms were refined anisotropically and hydrogen atoms placed in idealized positions and refined using a riding model. Details can be obtained from the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk for CCDC accession numbers CCDC2154984-2154986.

Table S1. Crystal Data, Solution and Refinement Parameters.

	3	**MOF-1**	**MOF-2**
CCDC number	2154986	2154984	2154985
formula	$C_{68}H_{108}N_2O_{20}$	$C_{80}H_{108}N_6O_{20}Zn_2$	$C_{61}H_{89}N_2O_{22}Zn_2$
formula weight	1273.56	1604.46	1333.08
T(K)	149.99(10)	100.0	150.0
crystal system	triclinic	monoclinic	monoclinic
space group	*P*-1	$P2_1/c$	$C2/c$
a (Å)	13.1611(2)	14.5555(8)	40.094(2)
b (Å)	14.9762(3)	14.5616(8)	13.0784(10)
c (Å)	19.1811(4)	19.0686(10)	18.2044(11)
α (º)	78.268(2)	90	90
β (º)	81.410(2)	93.536(2)	109.282(3)
γ (º)	77.789(2)	90	90
V (Å^3)	3595.52(12)	4033.9(4)	9010.3(10)
Z	2	2	4
ρ, g/cm^{-3}	1.176	1.321	0.983
μ, mm^{-1}	0.701	0.834	0.696
reflections used	14572	6877	7169
restraints	37	64	541
variables	865	507	403
R_1 [$I > 2\sigma(I)$][a]	0.0846	0.1022	0.1076
R_1 (all data)	0.0951	0.1308	0.1755
R_2w [$I > 2\sigma(I)$][b]	0.2435	0.2897	0.2872
R_2w (all data)	0.2576	0.3228	0.3529
GoF on F^2	1.015	1.280	0.955

[a] $R_1 = \Sigma \, ||F_o| - |F_c|| \, / \, \Sigma \, |F_o|$; [b] $R_2w = [\Sigma[w(F_o^2 - F_c^2)^2] \, / \, \Sigma[w(F_o^2)^2]]^{1/2}$, where $w = q[\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$

5. Powder X-ray diffraction of MOF-1 and MOF-2

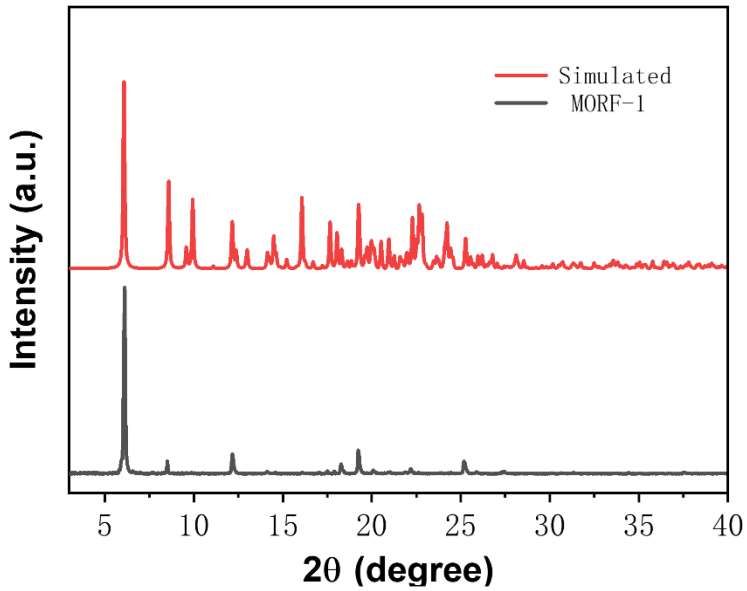


Figure S2. Powder X-Ray Diffraction pattern of as-prepared **MOF-1** (black) and Simulated (red)

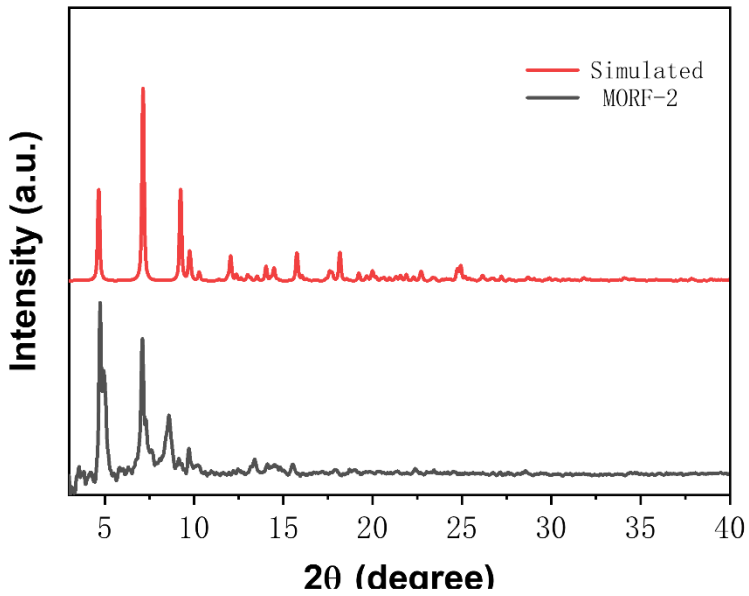


Figure S3. Powder X-Ray Diffraction pattern of as-prepared **MOF-2** (black) and Simulated (red)

6. Thermogravimetric analysis (TGA) of MOF-1 and MOF-2

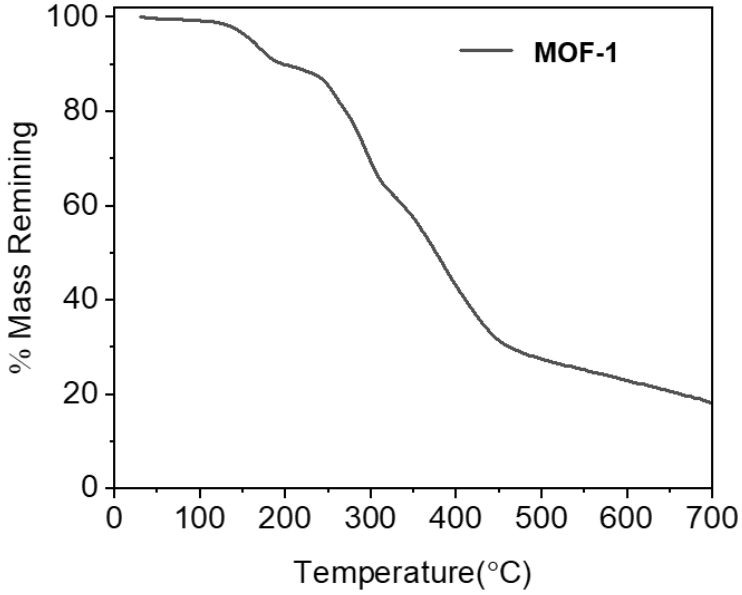


Figure S4. Thermogravimetric analysis (TGA) of as-synthesized **MOF-1**.

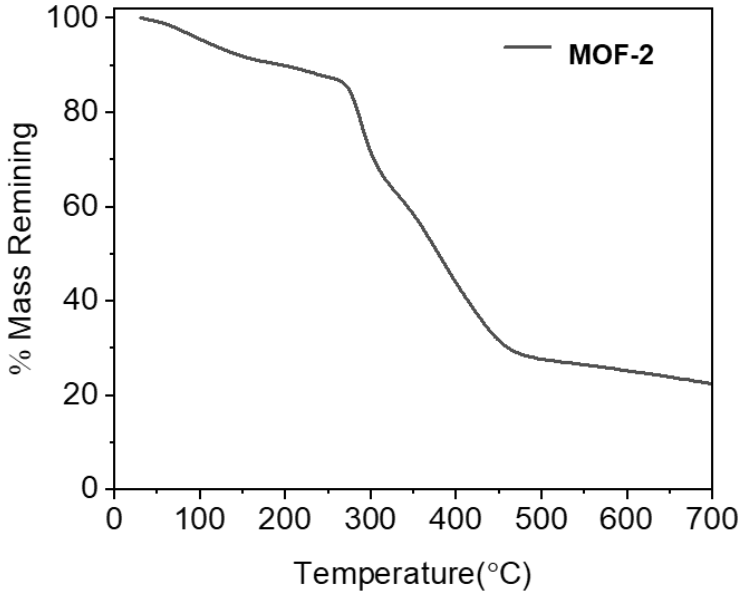


Figure S5. Thermogravimetric analysis (TGA) of as-synthesized **MOF-2**.

7. Infrared spectroscopy (IR) of MOF-1 and MOF-2

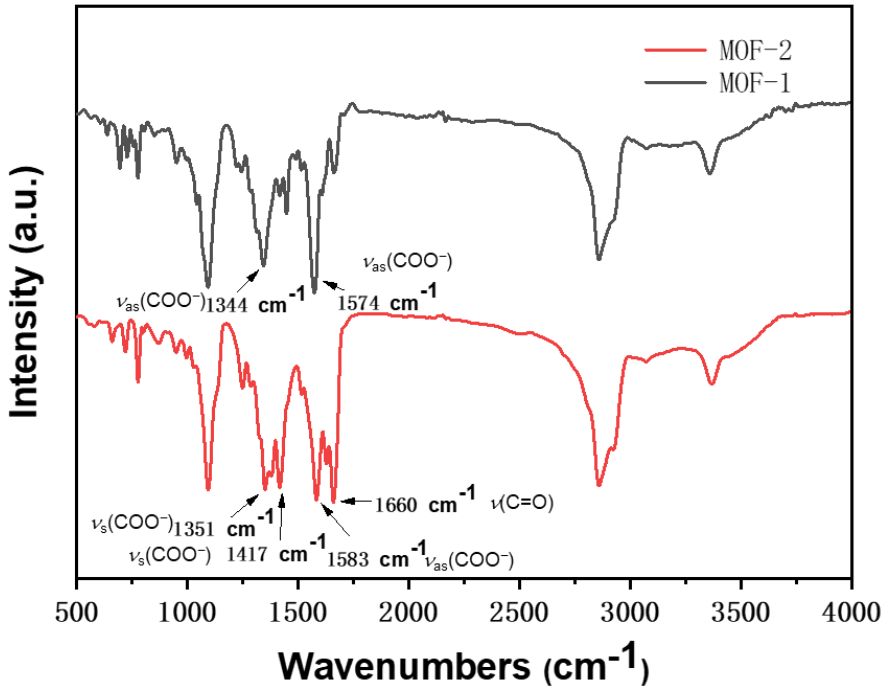


Figure S6. Infrared spectra of as-synthesized **MOF-1** (black) and **MOF-2** (red). $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ represent antisymmetric and symmetric vibration modes for carboxylates in MOFs. Band at 1660 cm^{-1} is attributed to ν(C=O) of residual DMF.

8. NMR spectra of compounds

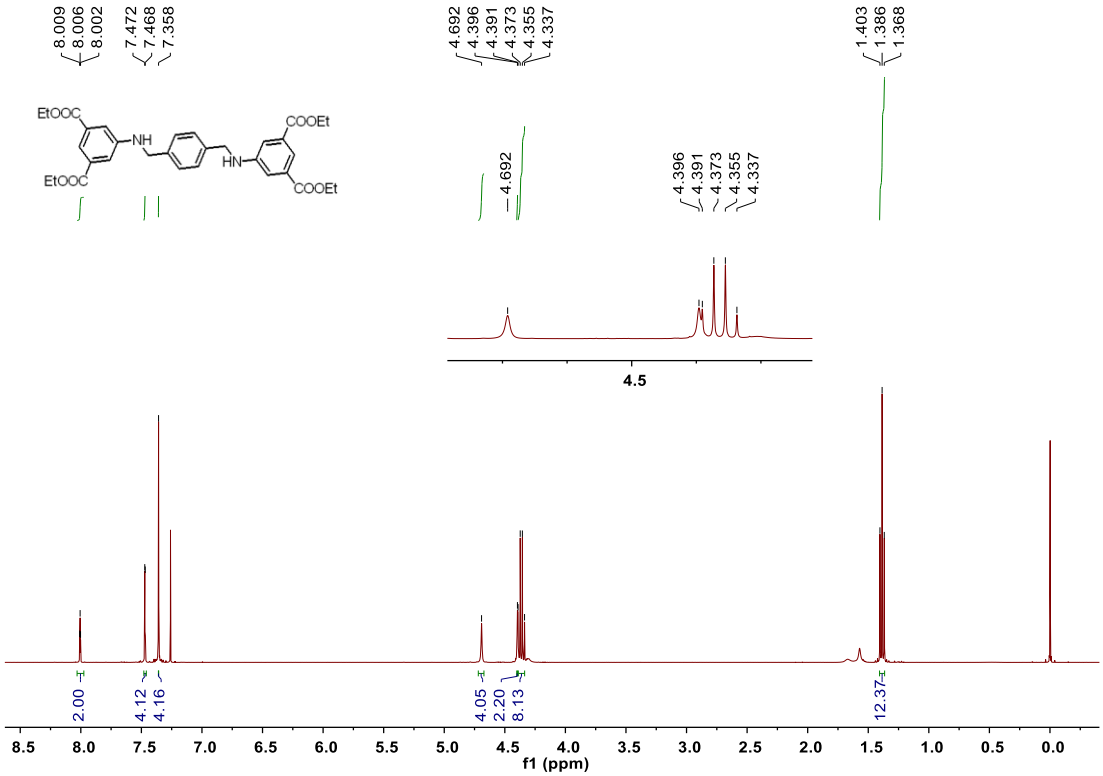


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **1**.

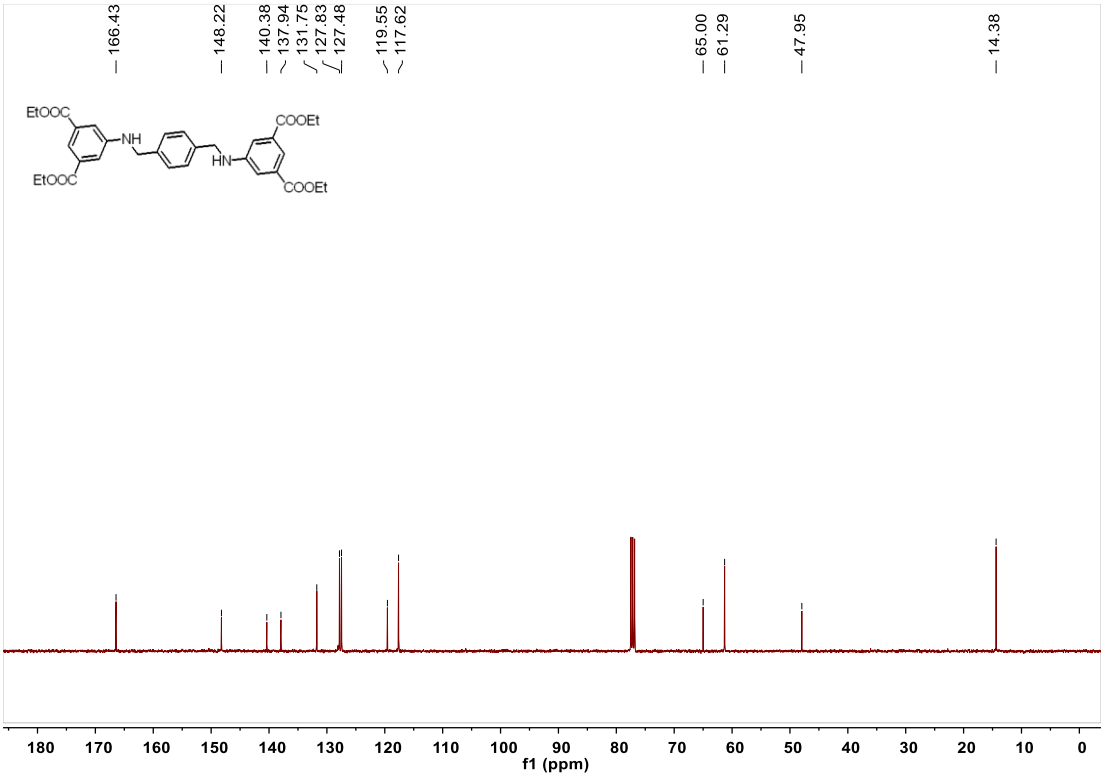


Figure S8. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of compound **1**.

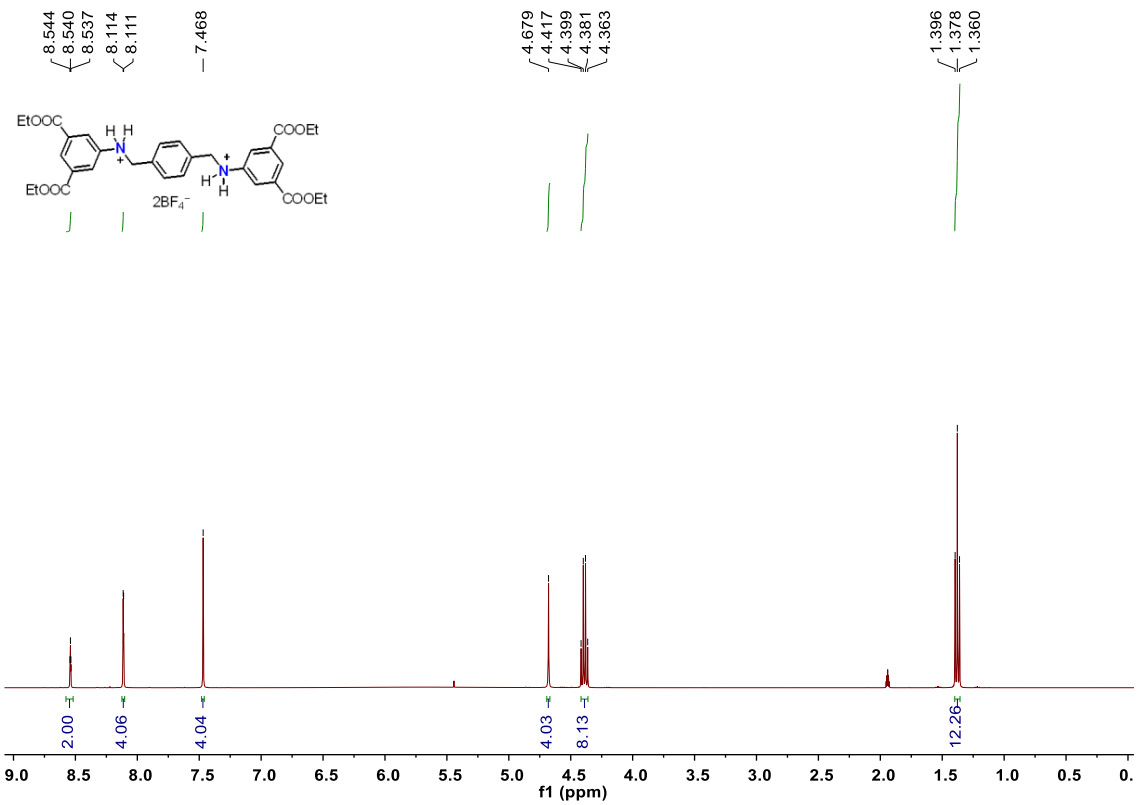


Figure S9. ^{1}H NMR (400 MHz, CD_3CN) spectrum of compound [**2**-H_2][BF_4]$_2$.

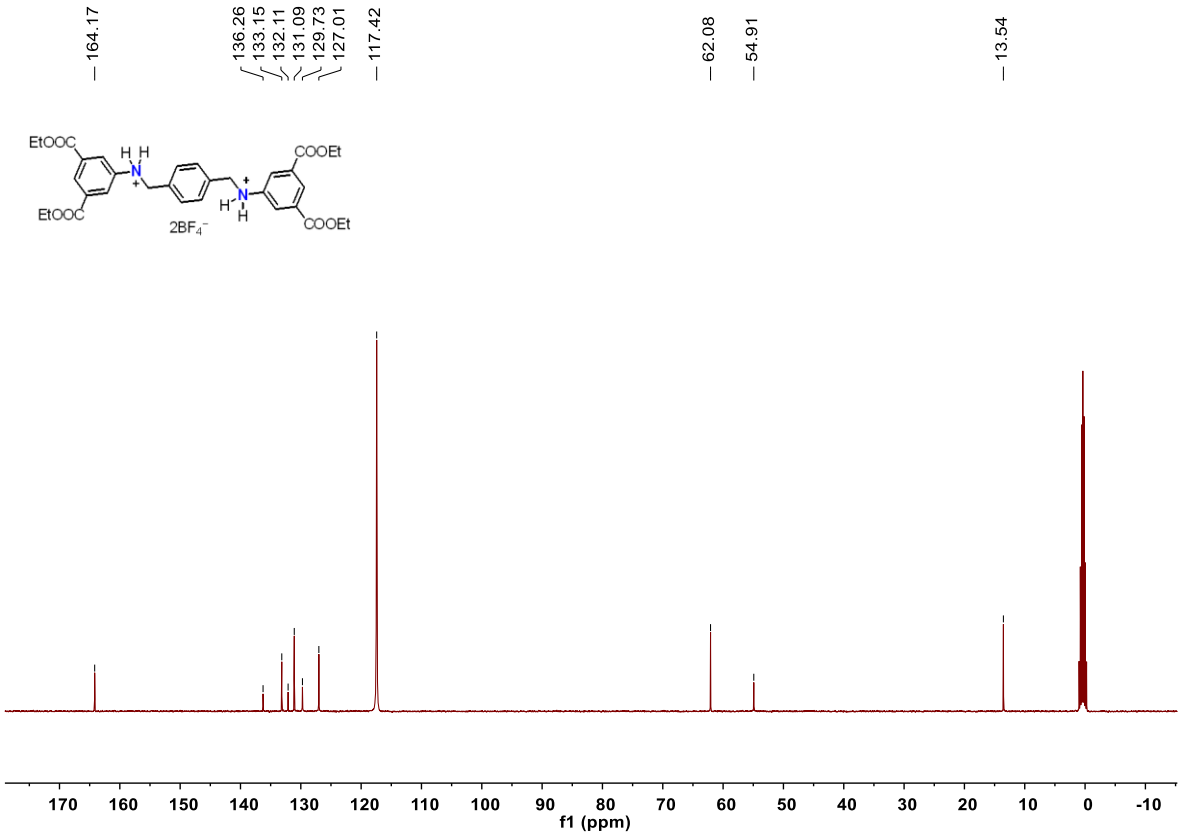


Figure S10. ^{13}C NMR (400 MHz, CD_3CN) spectrum of compound [**2**-H_2][BF_4]$_2$.

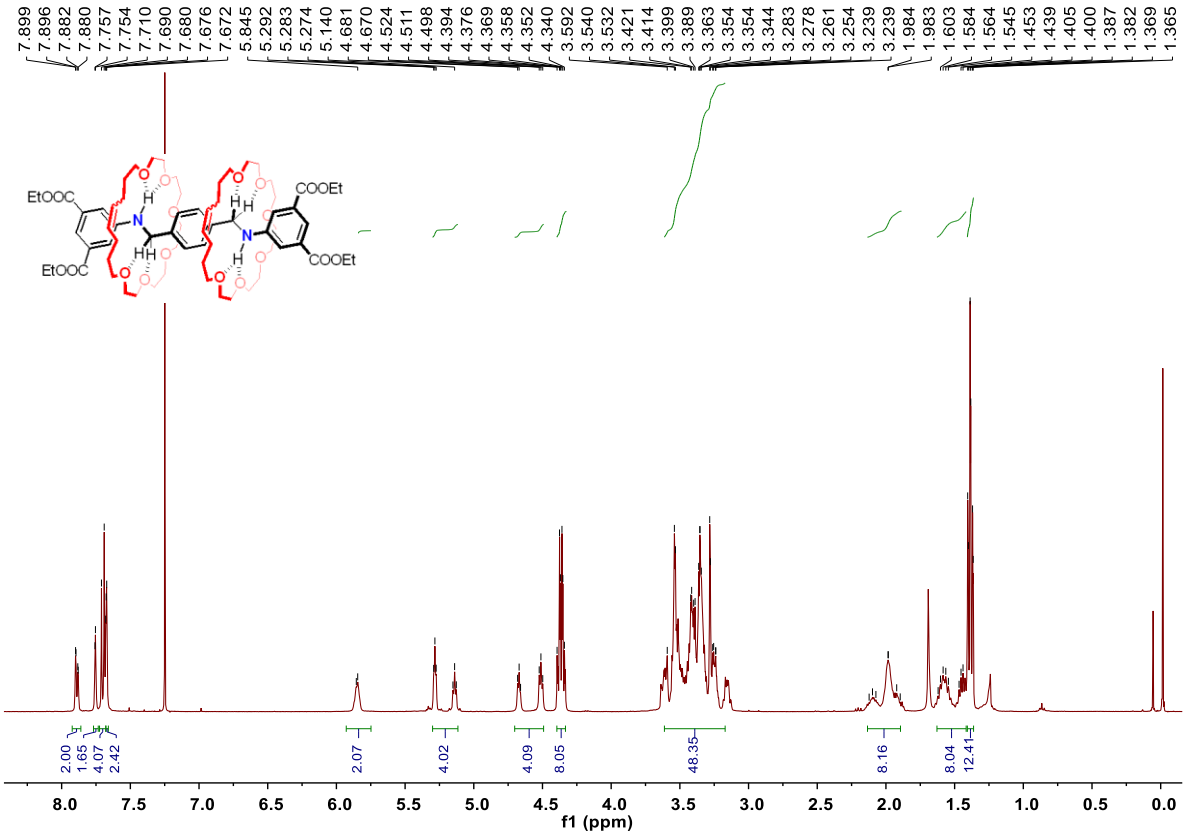


Figure S11. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3′**.

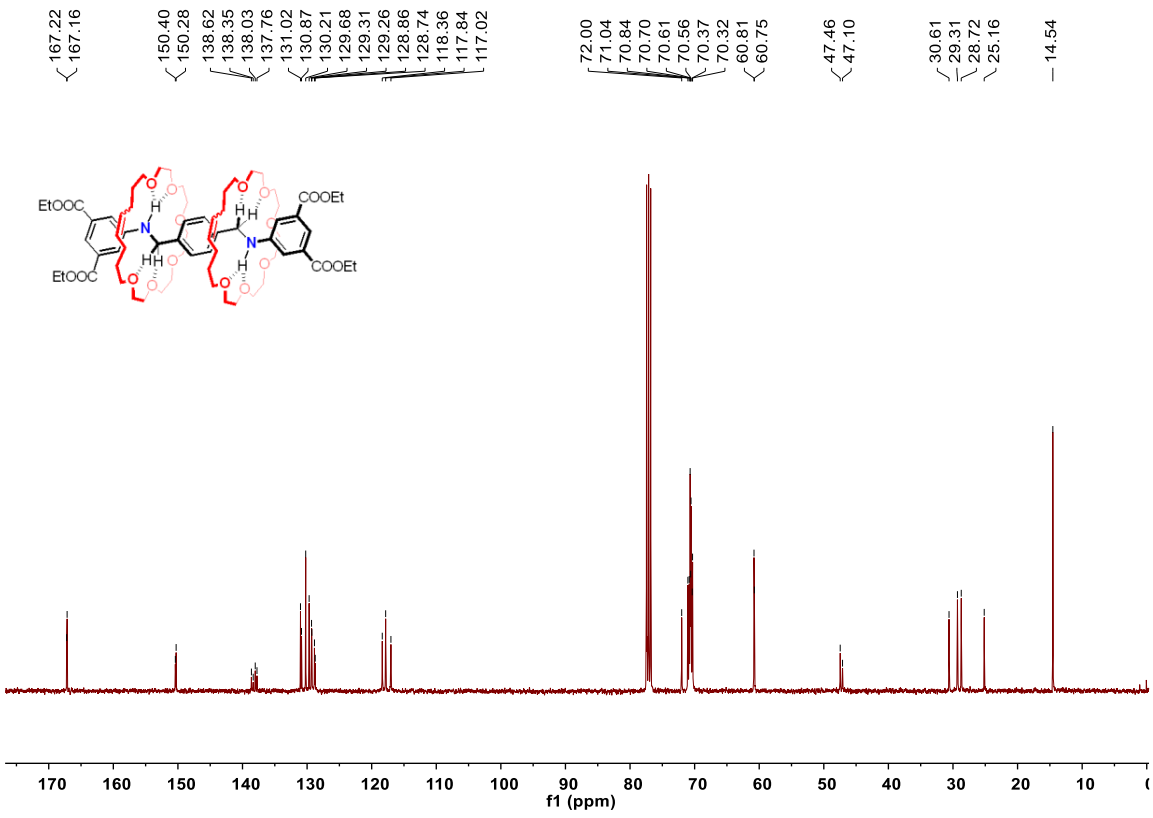


Figure S12. ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of compound **3′**.

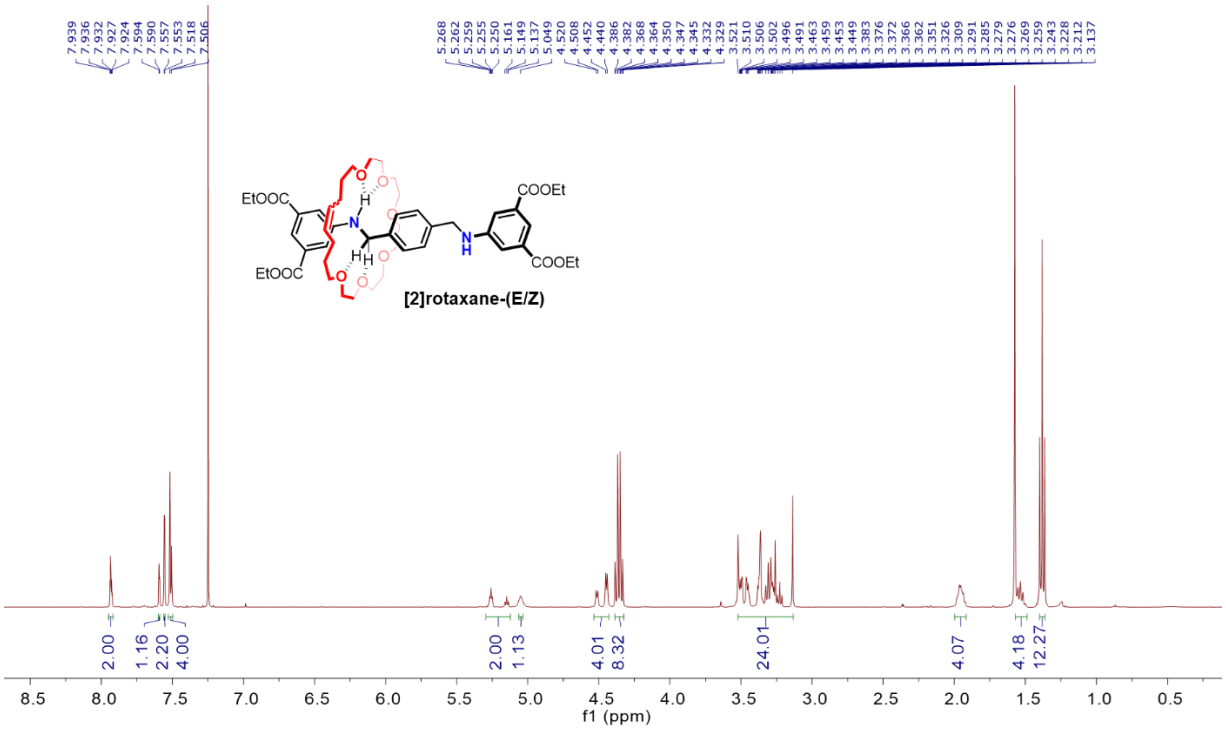


Figure S13. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of [2]rotaxane-(*E/Z*).

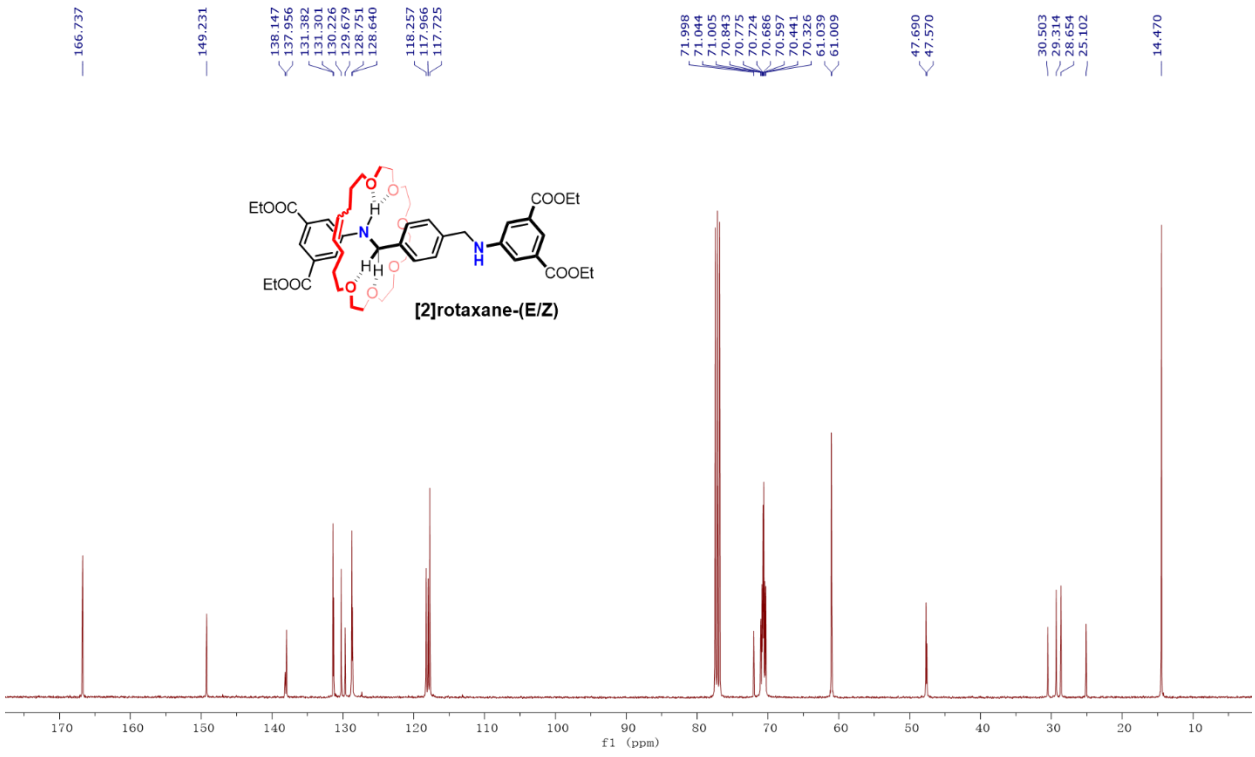


Figure S14. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of [2]rotaxane-(*E/Z*).

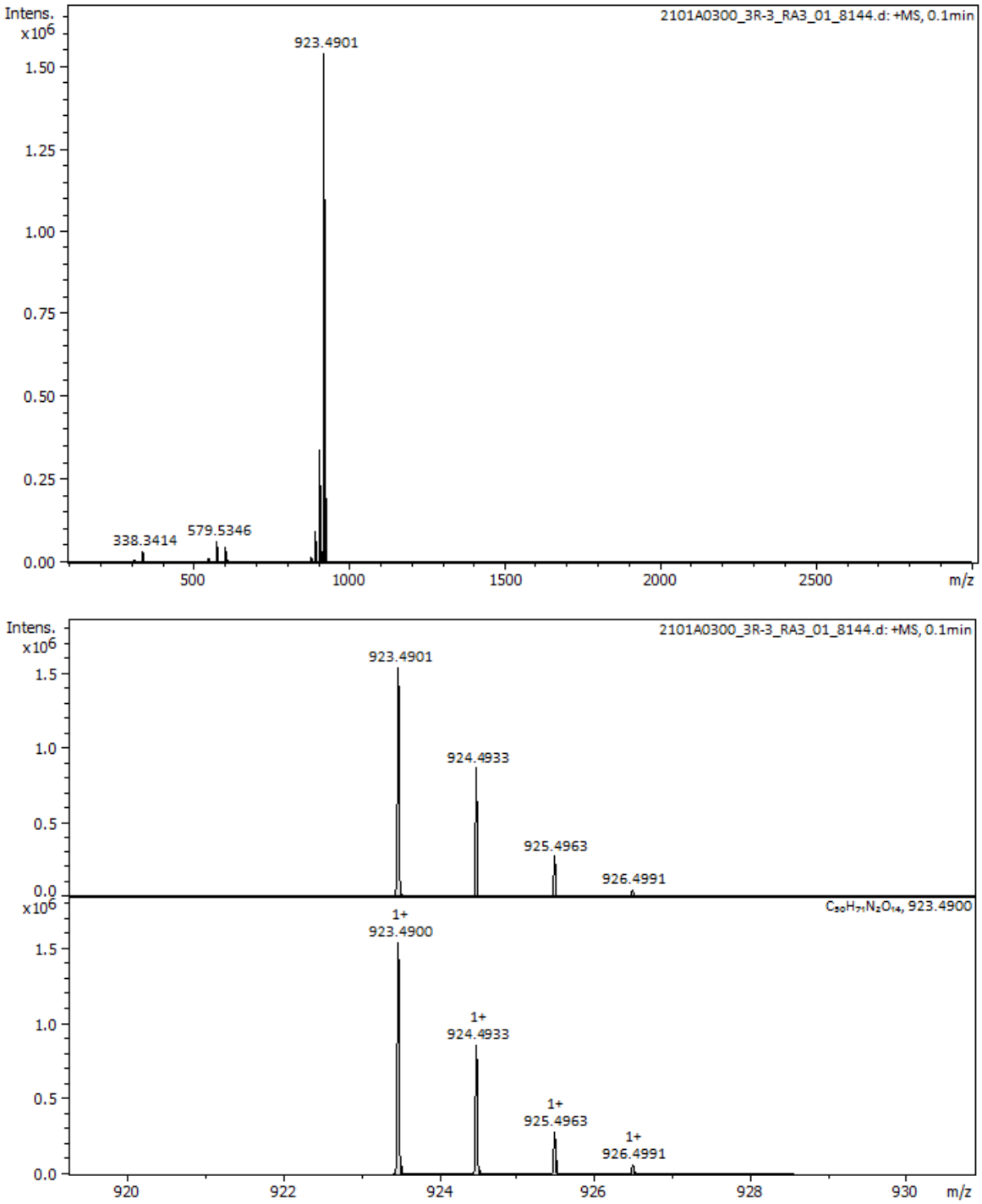


Figure S15. High-resolution mass spectroscopy (HRMS) of the [3]rotaxane linker $\mathbf{L_{Rot}}$. Full range of the spectrum (top) and the comparison of simulated and observed isotope patterns of fragment peak $[\mathbf{L}+H]^+$ (bottom).

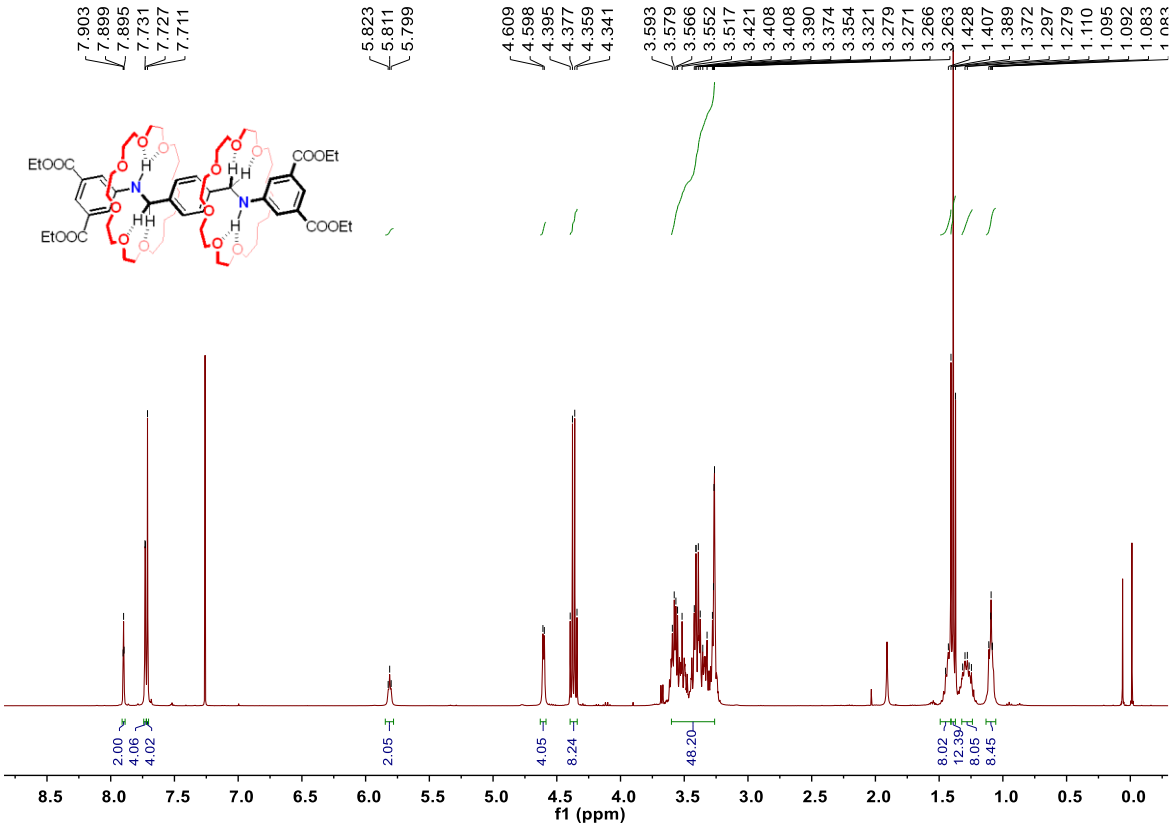


Figure S16. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3**.

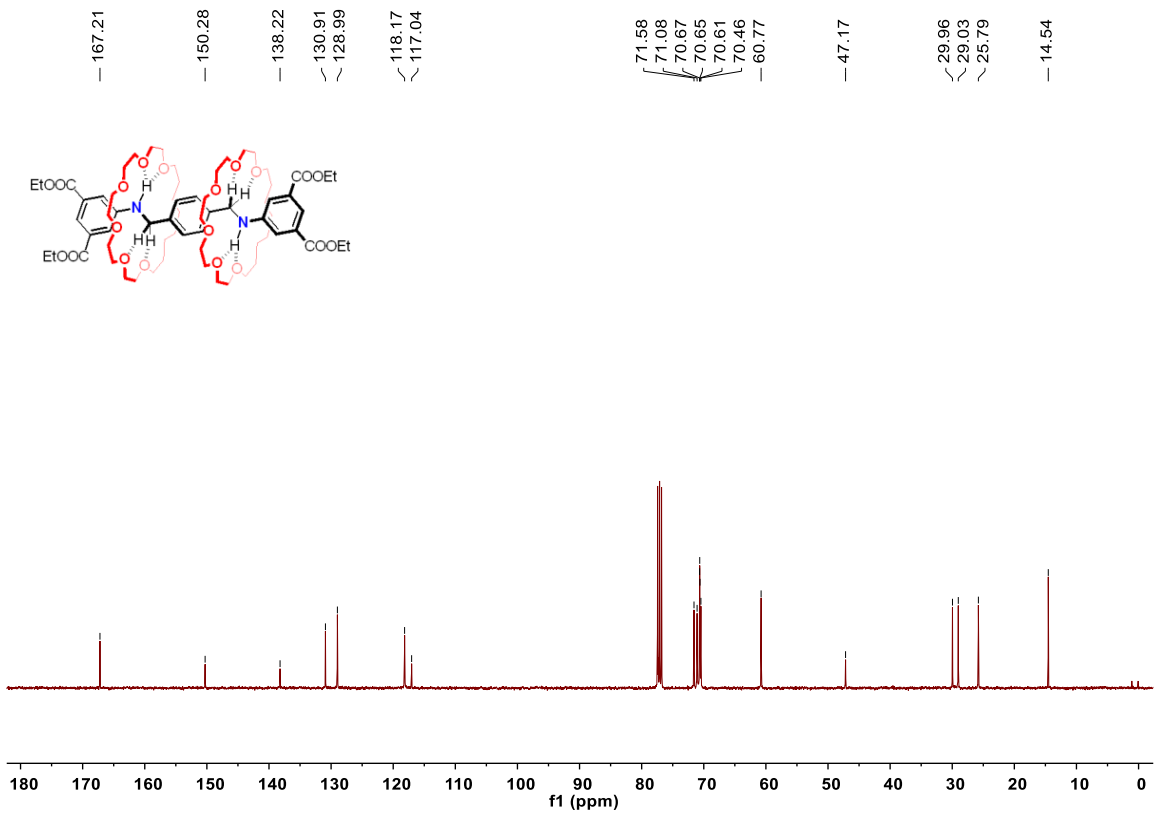


Figure S17. ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of compound **3**.

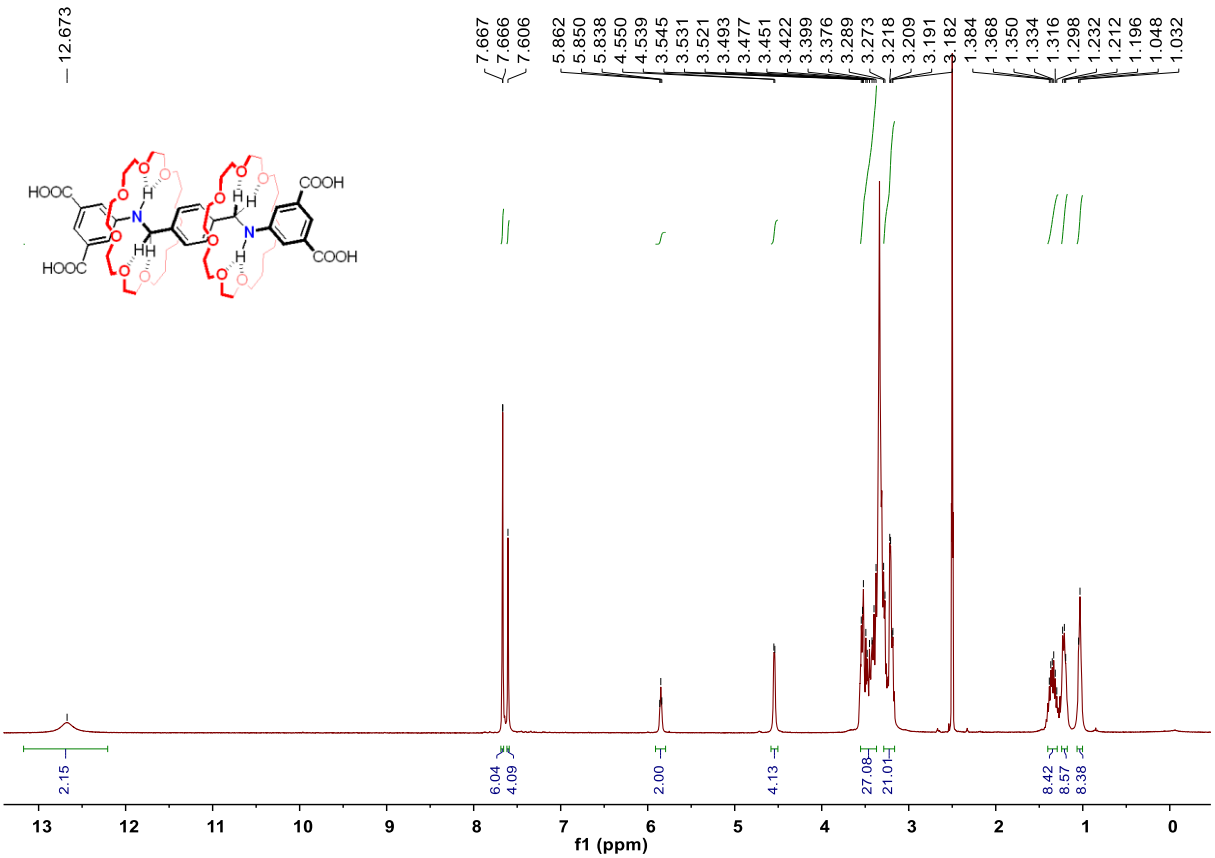


Figure S18. ^{1}H NMR (400 MHz, DMSO-D_6) spectrum of compound **H_4L^{Rot}**.

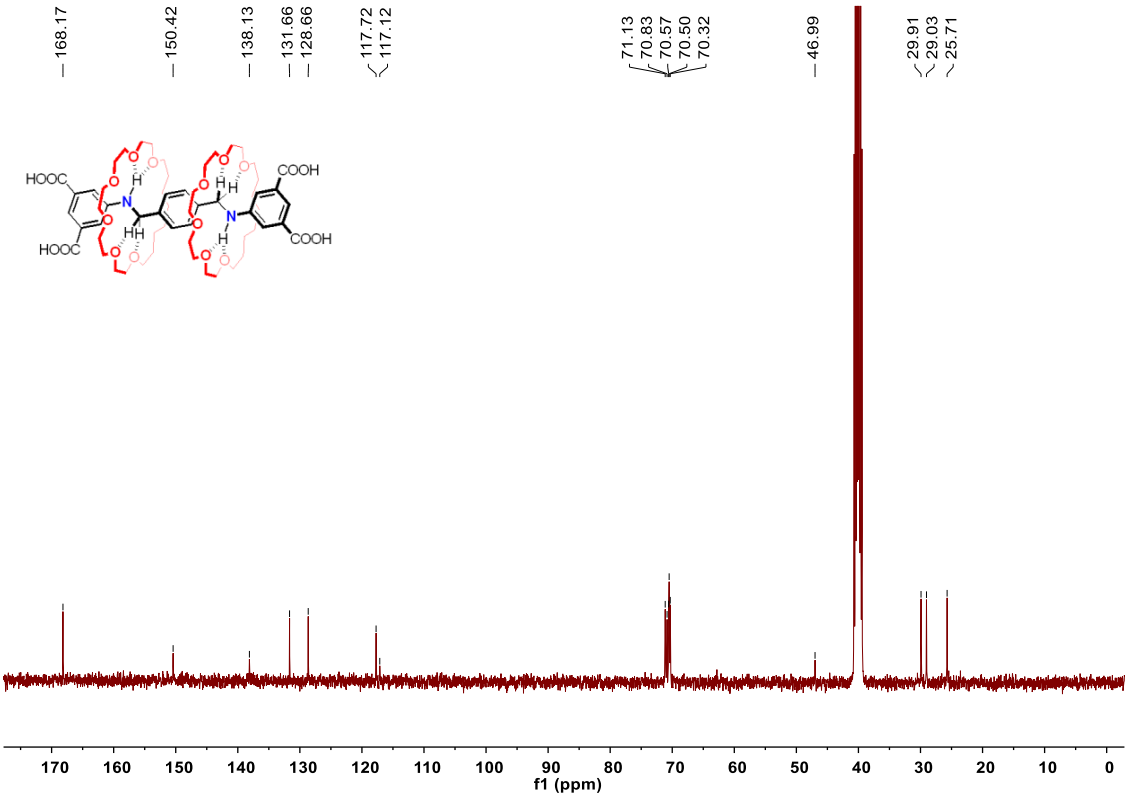


Figure S19. ^{1}H NMR (400 MHz, DMSO-D_6) spectrum of compound **H_4L^{Rot}**.

Reference:

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