Electronic Supplementary Material (ESI) for ChemComm.

Pillar[5]arene-based [1]rotaxanes with salicylaldimine as the stopper: syntheses, characterizations and application in the fluorescence turn-on sensing of Zn^{2+} in water

Longtao Ma,[1,2,§] Ruowen Tang,[1,§] Youjun Zhou,[1] Jiali Bei,[1] Yang Wang,[1,*] Tingting Chen,[1,*] Changjin Ou,[1] Yang Wang*, Ying Han,[2,*] Chaoguo Yan,[2] and Yong Yao[1,*]

[1]*School of Chemistry and Chemical Engineering, Nantong University, Nantong, Jiangsu, 226019, P. R. China.*

[2]*School of Chemistry and Chemical Engineering, Yangzhou University, Yangzhou, Jiangsu, 225001, P.R. China.*
Email: ywang85@ntu.edu.cn; ttchen1980@126.com; Hanying@yzu.edu.cn; yaoyong1986@ntu.edu.cn

Supporting Information (23 pages)

1. Materials and methods

Materials

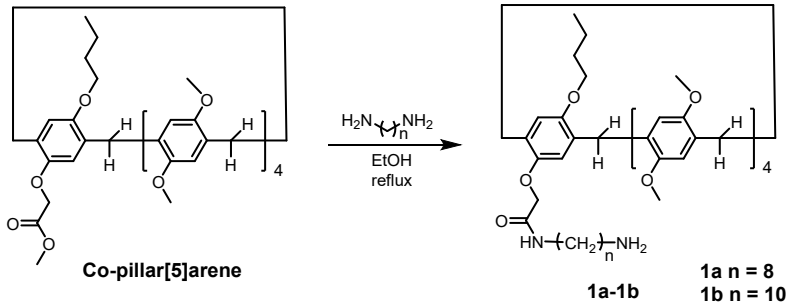
All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. Pillar[5]arene P5 was prepared according previous report.[S1,S2]

Measurements

^{1}H NMR and ^{13}C HMR spectra were recorded with a Bruker Avance DMX-400 spectrometer or a Bruker Avance DMX-600 spectrometer using the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. NOESY spectra were collected on a Bruker Avance DMX-500 or Bruker Avance DMX-600 spectrometer with internal standard TMS. High-resolution mass spectrometric experiments were performed with a Bruker 7-Tesla FT-ICR mass spectrometer equipped with an electrospray source (Billerica, MA, USA). Steady-state fluorescence spectra were recorded in a conventional quartz cell (light path 10 mm) on a Varian Cary Eclipse equipped with a Varian Cary single-cell peltier accessory to control temperature. Single crystal data was collected by Bruker AXS (SMART APEX II) Instrument.

2. Syntheses of 1a and 1b

Scheme S1. Synthetic route of **1a** and **1b**



Synthesis of compound **1**: A suspension of monoester copillar[5]arene (2.0 mmol, 1.70 g) and excess of α,ω-diaminoalkanes (80 mmol) in ethanol (20 mL) was refluxed for 8 hours. After cooling, the resulting precipitate was collected by filtration and washed with cold ethanol to give the white solid (**1a** and **1b**) for analysis.

1a: White solid, 50%, m.p.155-157°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.93 – 6.82 (m, 9H, ArH), 6.74 (d, *J* = 7.7 Hz, 1H, ArH), 5.19 (s, 1H, NH), 4.57 (s, 2H, CH_2), 3.89 (m, 3H, CH_2), 3.80 – 3.71 (m, 34H, 8 OCH_3, 5 CH_2), 3.63 (s, 1H, CH_2), 2.66 (t, *J* = 7.2 Hz, 2H, CH_2), 1.88 – 1.81 (m, 2H, CH_2), 1.61 (m, 2H, CH_2), 1.23 (m, 2H, CH_2), 1.04 (t, *J* = 7.4 Hz, 3H, CH_3), 0.69 (m, 2H, CH_2), -0.12 (s, 2H, CH_2), -1.15 (s, 2H, CH_2), -1.39 (s, 2H, CH_2), -2.22 (s, 2H, CH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.3, 150.8, 150.4, 150.4, 150.3, 150.3, 150.2, 150.0, 147.0, 129.4, 129.1, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.3, 126.9, 114.9, 114.1, 113.9, 113.5, 112.8, 112.7, 112.5, 112.4, 68.0, 66.0, 55.7, 55.6, 55.5, 55.4, 55.3, 55.1, 42.8, 38.0, 34.8, 32.1, 30.1, 29.3, 29.2, 28.9, 28.6, 28.5, 28.4, 27.7, 26.7, 23.7, 19.6, 14.1; IR(KBr) υ: 3404.05, 2932.50, 2855.13, 2482.04, 2145.84, 2039.04, 1678.90, 1610.10, 1500.35, 1464.81, 1399.98, 1306.58, 1213.24, 1100.97, 1047.92, 928.69, 878.14, 854.71, 774.01, 704.73, 647.36, 604.78, 541.10, 454.15 cm^{-1}; MS (m/z): HRMS (ESI) Calcd. for $C_{57}H_{75}N_2O_{11}$([M + H]$^{+}$): 963.5371, found: 963.5392.

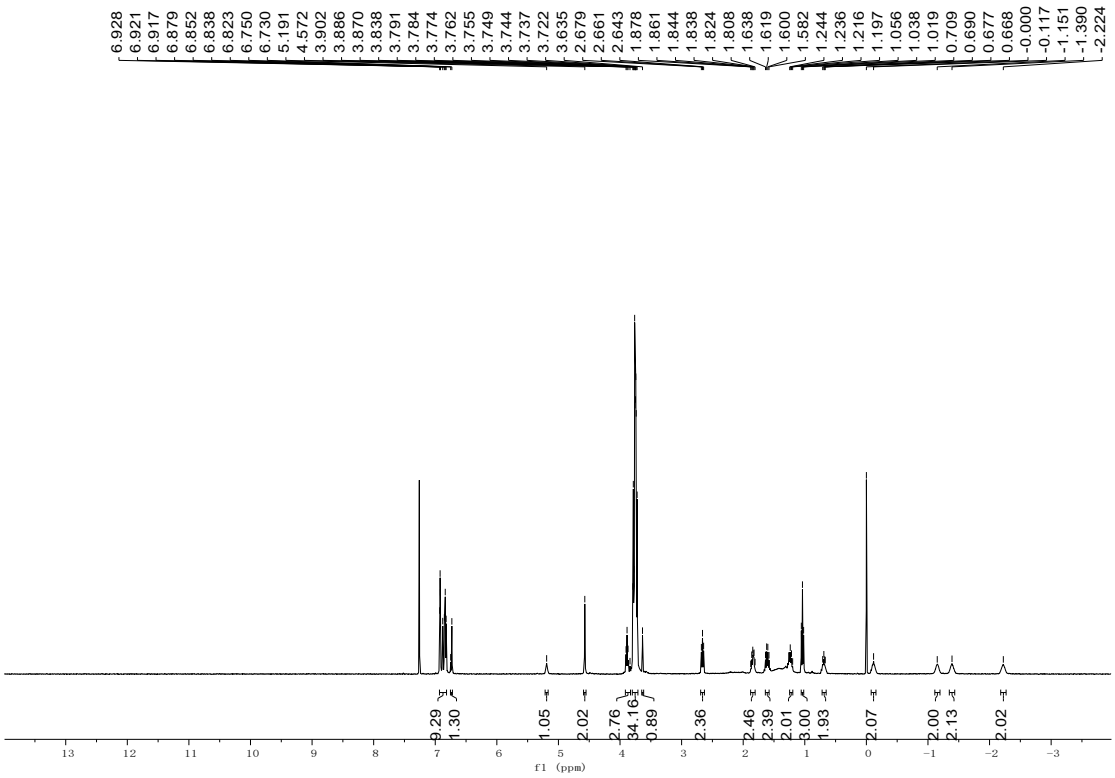


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293 K) of **1a**.

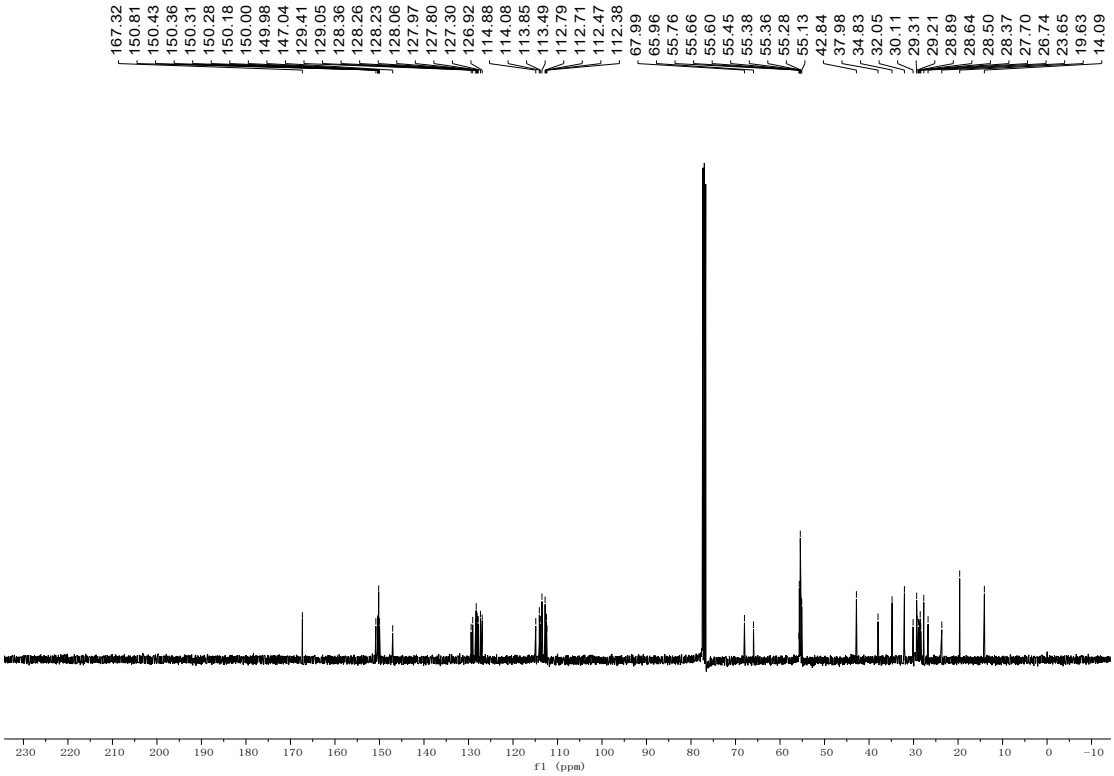


Figure S2. ^{13}C NMR spectrum ($CDCl_3$, room temperature, 100 MHz) of **1a**.

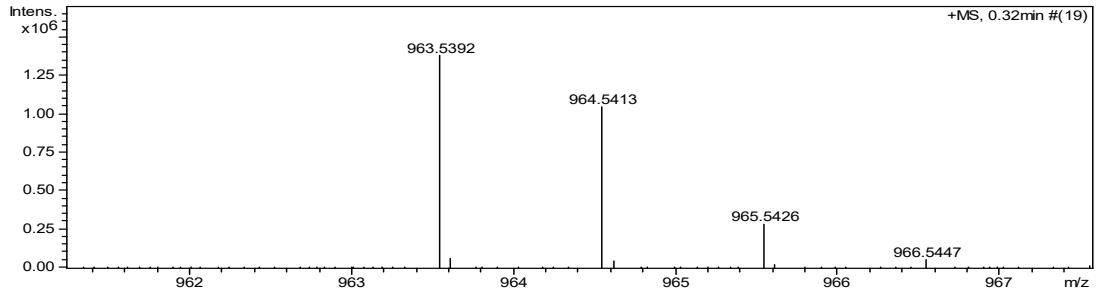


Figure S3. Mass spectra of **1a** Calcd. for $C_{57}H_{74}N_2O_{11}$([M + H]$^+$): 963.5371, found: 963.5392.

1b: White solid, 40%, m.p.130-131℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.94 – 6.82 (m, 9H, ArH), 6.72 (s, 1H, ArH), 5.10 (s, 1H, NH), 4.57 (s, 2H, CH_2), 3.88 (m, 3H, CH_2), 3.82 – 3.70 (m, 34H, 8 OCH_3, 5 CH_2), 3.64 (s, 1H, CH_2), 2.73 (t, *J* = 7.1 Hz, 2H, CH_2), 1.84 (t, *J* = 7.5 Hz, 2H, CH_2), 1.62 – 1.57 (t, J = 7.6 Hz, 2H, CH_2), 1.49 – 1.45 (t, J = 7.6 Hz, 2H, CH_2), 1.32 (d, *J* = 7.2 Hz, 2H, CH_2), 1.16 (d, *J* = 8.0 Hz, 2H, CH_2), 1.04 (t, *J* = 7.4 Hz, 3H, CH_3), 0.77 (s, 2H, CH_2), -0.06 (s, 2H, CH_2), -1.31 (s, 4H, CH_2), -2.29 (s, 2H, CH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.2, 150.8, 150.7, 150.4, 150.3, 150.1, 150.1, 150.0, 147.0, 129.4, 129.0, 128.3, 128.2, 128.1, 128.0, 127.8, 127.1, 126.8, 114.7, 114.0, 113.9, 113.6, 113.2, 112.8, 112.7, 112.5, 112.4, 67.8, 65.9, 55.4, 55.3, 55.2, 55.1, 42.4, 38.0, 34.2, 32.1, 30.9, 30.8, 29.7, 29.2, 28.9, 28.7, 28.3, 27.8, 26.5, 23.6, 19.6, 14.1; IR (KBr) υ: 3407.95, 2930.79, 2853.95, 2146.30, 2039.48, 1680.45, 1499.90, 1464.94, 1399.77, 1304.96, 1213.17, 1101.25, 1048.14, 929.12, 878.58, 855.36, 774.36, 704.94, 647.41, 606.87, 541.77, 451.37 cm^{-1}; MS (m/z): HRMS (ESI) Calcd. for $C_{59}H_{79}N_2O_{11}$([M + H]$^+$): 991.5684, found: 991.5709.

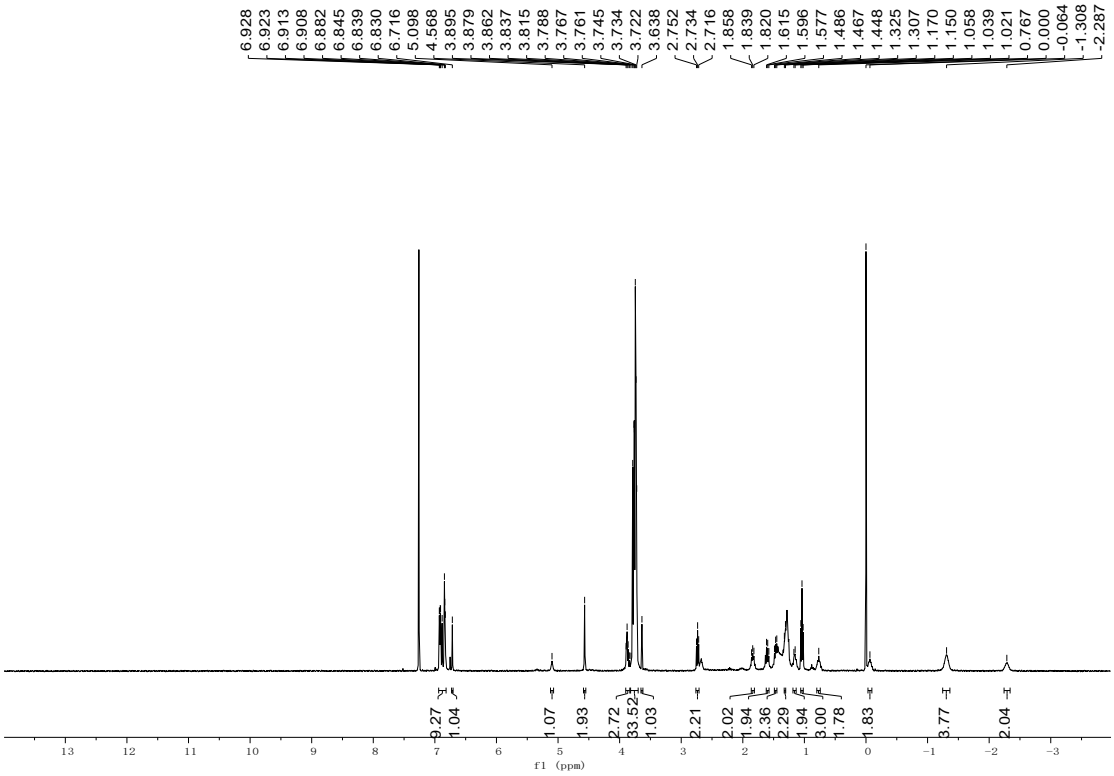


Figure S4 ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293 K) of **1b**.

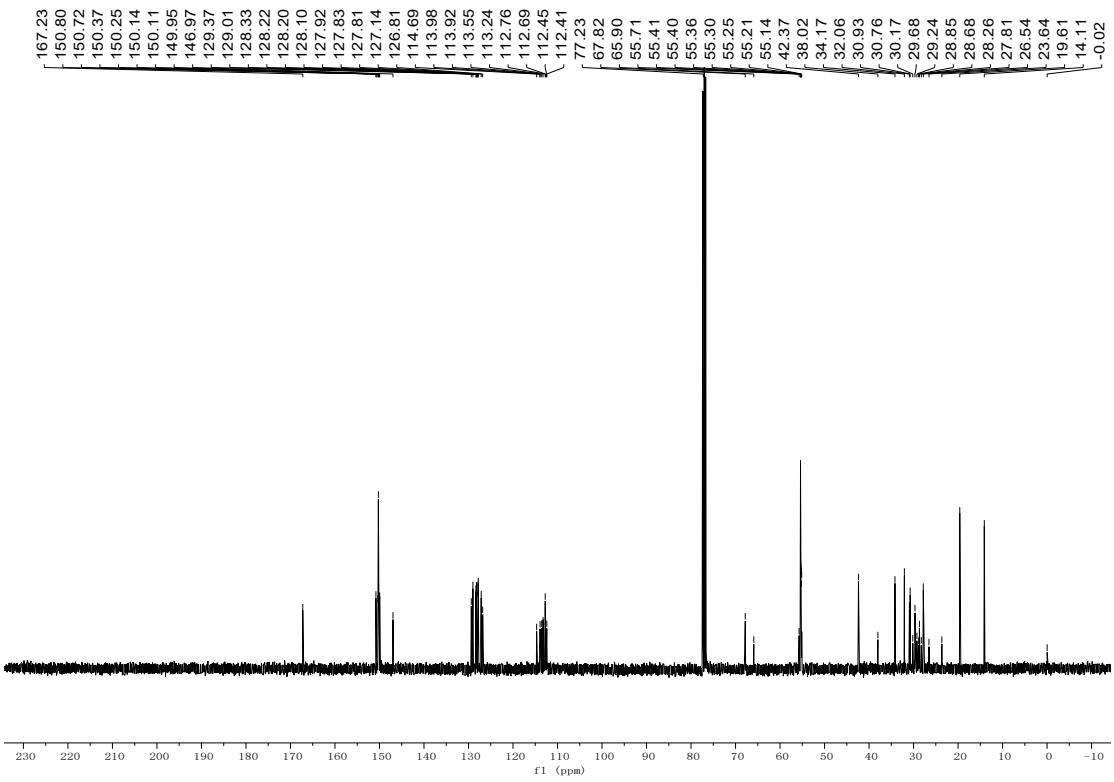


Figure S5 ^{13}C NMR spectrum ($CDCl_3$, room temperature, 100 MHz) of **1b**.

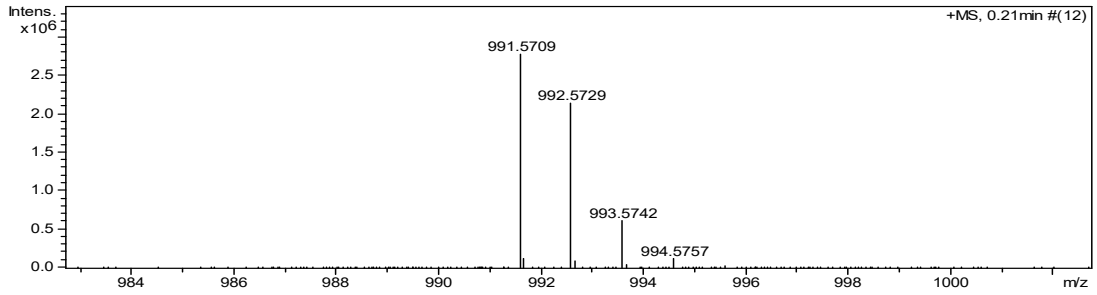
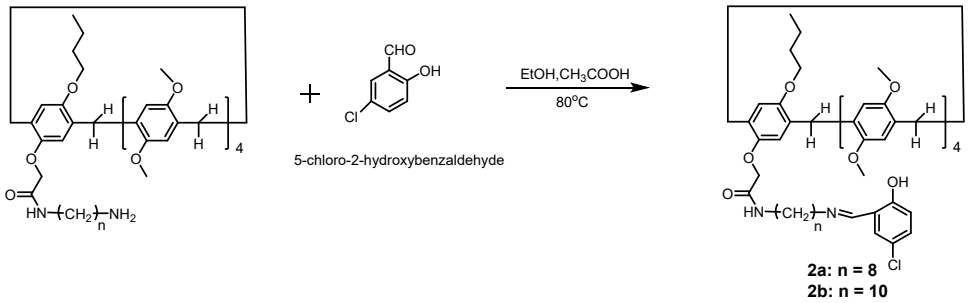


Figure S6 Mass spectra of **1b** Calcd. for $C_{59}H_{78}N_2O_{11}$([M + H]$^+$): 991.5684, found: 991.5709.

3. Syntheses of 2a and 2b



Scheme S2. Synthetic route of **2a** and **2b**

Synthesis of compound **2**: 0.33 mmol compound **1a** (or **1b**) was dissolved in 15 mL CH_3CH_2OH and heated to 80℃, then 2 drops of CH_3COOH and 0.3 mmol of 5-chloro-2-hydroxybenzaldehyde was added, the mixture was further reaction for 6h. After cooling, the resulting precipitate was collected by filtration and washed with cold ethanol to give the light yellow solid (**2a** and **2b**) for analysis.

2a：Yellow solid, 77%, m.p.107-108℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.48 (s, 1H, OH), 8.31 (s, 1H, CH), 7.27 (m, 2H, ArH), 6.98 – 6.81 (m, 10H, ArH), 6.72 (s, 1H, ArH), 5.09 (s, 1H, NH), 4.57 (s, 2H, CH_2), 3.87 (m, 2H, CH_2), 3.80 – 3.69 (m, 32H, $8OCH_3$,$4CH_2$), 3.58 (t, *J* = 7.2 Hz, 2H, CH_2), 2.48 (s, 2H, CH_2), 1.81 (t, 2H, CH_2), 1.53 (m, 4H, CH_2), 0.99 (t, *J* = 7.4 Hz, 3H, CH_3), 0.81 (d, *J* = 10.9 Hz, 2H, CH_2), -0.10 (s, 2H, CH_2), -1.33 (s, 4H, CH_2), -2.28 (s, 2H,CH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 167.3, 163.3 , 159.9, 150.8, 150.4, 150.4, 150.3, 150.3, 150.2, 150.1, 150.0, 147.1, 132.1, 130.1, 129.5, 129.1, 128.4, 128.3, 128.2, 128.1, 127.9, 127.9, 127.3, 126.9, 123.2, 119.4, 118.7, 115.0, 114.1, 113.7, 113.5, 113.5, 112.8, 112.4, 68.1, 65.9, 60.3, 55.7, 55.6, 55.4, 55.3, 55.1, 38.1, 32.1, 31.8, 30.2, 29.3, 29.2, 28.9, 28.7, 28.5, 28.3, 28.1, 26.3, 23.6, 19.6, 14.1; IR (KBr) υ: 3410, 2935, 2840, 2481, 2143, 2037, 1738, 1680, 1634, 1498, 1398, 1284, 1211, 1044, 926, 872, 822, 772, 705, 644, 553, 454 cm^{-1}; MS (m/z): HRMS (ESI) Calcd. for $C_{64}H_{77}ClN_2O_{12}Na$ ([M + Na]$^{+}$): 1123.5063, found: 1123.5039.

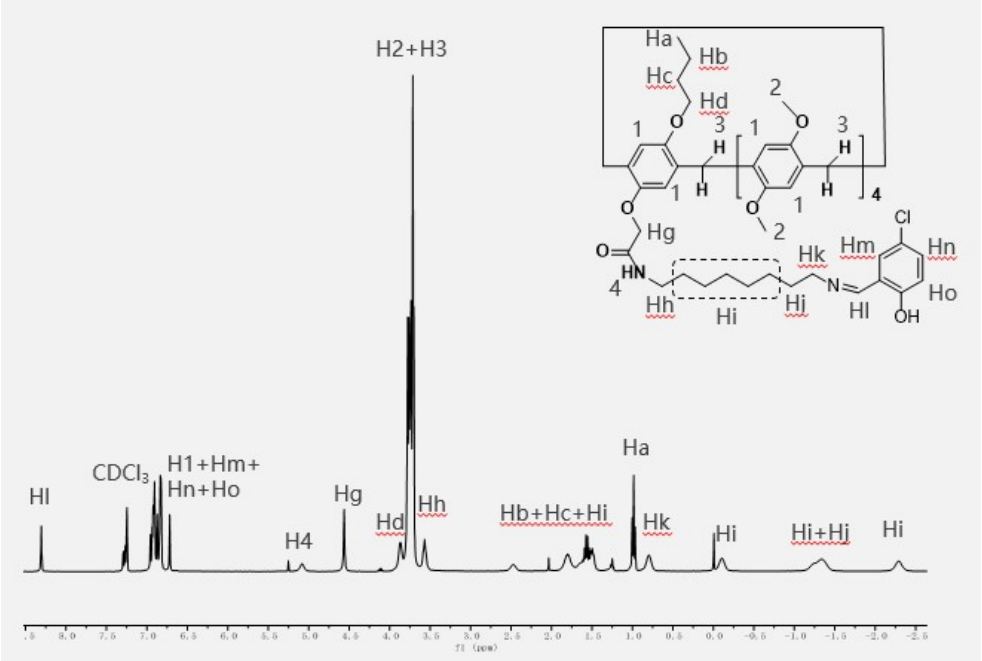


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293 K) of **2a**.

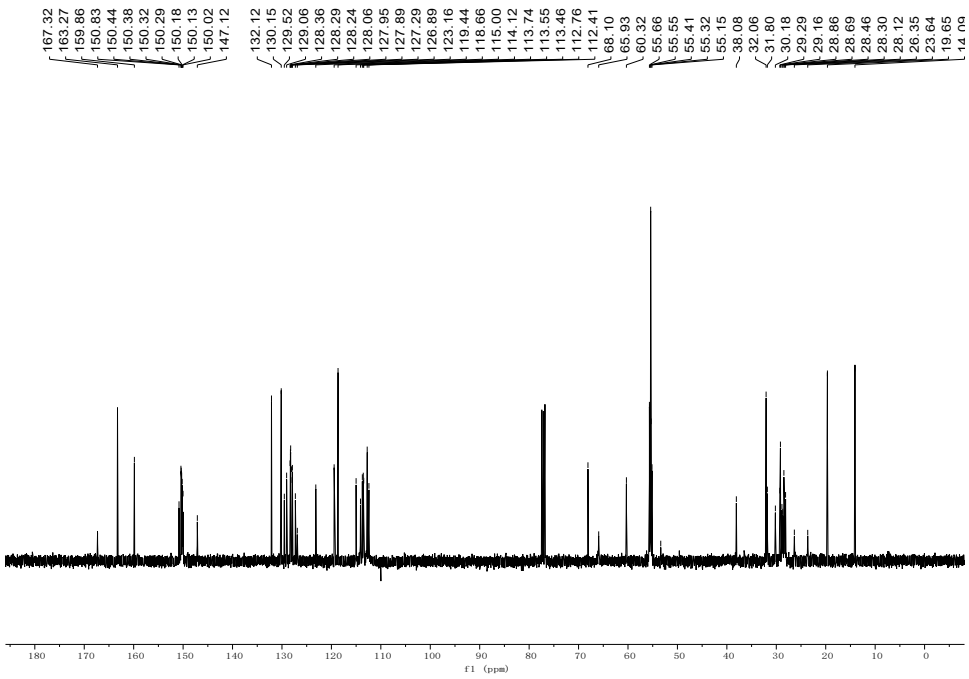


Figure S8. ^{13}C NMR spectrum ($CDCl_3$, room temperature, 100 MHz) of **2a**.

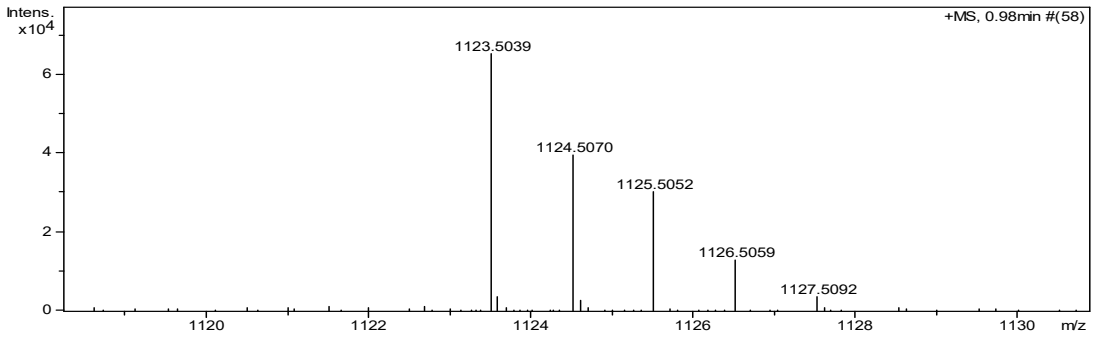


Figure S9 Mass spectra of **2a** Calcd. for $C_{64}H_{77}ClN_2O_{12}$([M + Na]$^+$): 1123.5063, found: 1123.5039.

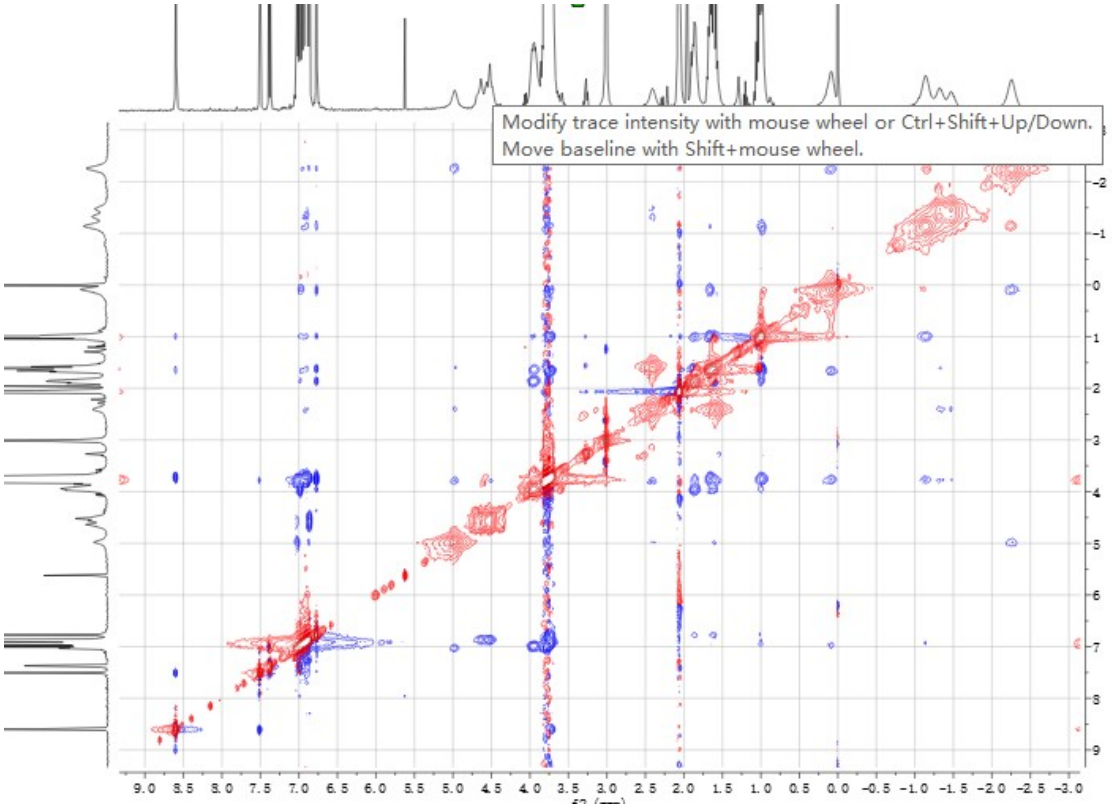


Figure S10. 2D NMR of **2a**.

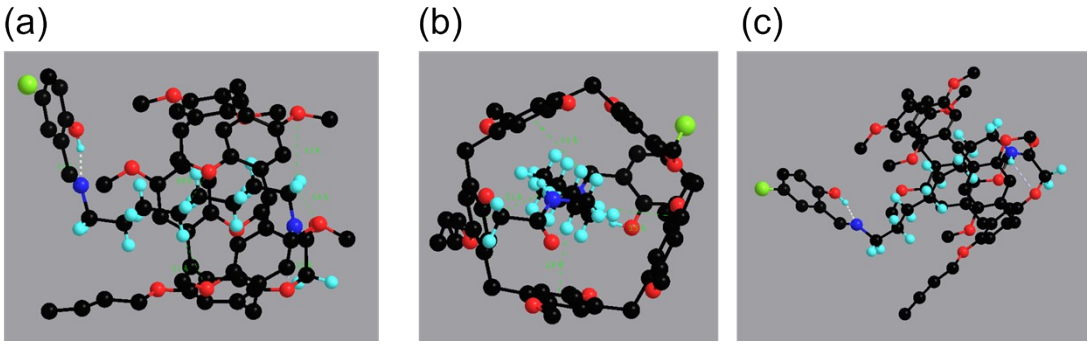


Figure S11. Ball and stick views of the X-ray single-crystal structure of [1]rotaxane **2a**. (a) C–H···O interactions. (b) C–H···π interactions. (c) N–H···O and O–H···N hydrogen bondings.

Table S1 Information of crystal data for 2a

Phase	
Empirical formula	$C_{64}H_{77}ClN_2O_{12}$
Formula weight	1101.72
Temperature(K)	296(2)
Wavelength(Å)	0.71073
Crystal system,	Monoclinic
space group	P2(1)/n
a(Å)	12.4109(17)
b(Å)	19.955(3)
c(Å)	25.114(4)
α(°)	90
β(°)	96.541(4)
γ(°)	90
Volume(Å^3)	6179.1(16)
Z	4
Calculated density(Mg·m^{-3})	1.184
Absorption coefficient(mm^{-1})	0.122
F(000)	2352
Crystal size(mm)	0.220 x 0.200 x 0.180
Theta range for data collection(°)	2.032 to 24.999
hkl ranges	-14 to 14, -23 to 23, -29 to 27
Reflections collected	62354 / 10837
unique	R(int)= 0.1423
Completeness to theta	99.7%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10837 / 36 / 722
Goodness-of-fit on F^2	0.961
Final R indices [I>2σ(I)]	R_1= 0.0881, wR_2= 0.2210
R indices (all data)	R_1= 0.2344, wR_2= 0.2629
Largest diff. peak and Hole(e·Å^3)	0.435 and -0.417

2b: Yellow solid, 77%, m.p.86-87°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 13.54 (s, 1H, OH), 8.32 (s, 1H, CH), 7.30 – 7.26 (t, J = 2.4Hz, 1H, ArH), 7.25 (d, *J* = 2.4 Hz, 1H, ArH), 6.95 – 6.87 (m, 6H, ArH), 6.85 – 6.82 (t, J = 3.6Hz, 4H, ArH), 6.71 (s, 1H, ArH), 5.06 (s, 1H, NH), 4.57 (s, 2H, CH_2), 3.87 (m, 2H, CH_2), 3.79 – 3.71 (m, 34H, 8OCH_3, 5CH_2), 3.65 (t, *J* = 6.8 Hz, 2H, CH_2), 2.46 (s, 2H, CH_2), 1.83 (s, 2H, CH_2), 1.73 (t, *J* = 7.8 Hz, 2H, CH_2), 1.62 (s, 1H, CH_2), 1.57 (d, *J* = 7.4 Hz, 1H, CH_2), 1.39 (t, *J* = 7.8 Hz, 2H, CH_2), 1.19 (t, *J* = 7.8 Hz, 2H, CH_2), 1.01 (t, *J* = 7.4 Hz, 3H, CH_3), 0.77 (s, 2H, CH_2), -0.08 (s, 2H, CH_2), -1.37 (s, 4H, CH_2), -2.35 (s, 2H, CH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 163.5, 159.9, 150.8, 150.4, 150.3, 150.3, 150.1, 150.0, 132.0, 130.2, 129.4, 129.0, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 127.2, 126.8, 123.1, 119.5, 118.6, 114.7, 114.0, 113.6, 113.3, 112.7, 112.4, 67.8, 65.9, 59.7, 55.5, 55.4, 55.4, 55.3, 55.1, 38.0, 32.1, 31.2, 30.8, 30.6, 30.2, 29.7, 29.3, 28.8, 28.6, 28.3, 28.1, 26.5, 23.6, 19.6, 14.1; IR(KBr) υ: 3410, 2935, 2841, 2038, 1680, 1633, 1499, 1462, 1398, 1283, 1210, 1044, 928, 872, 822, 772, 708, 642, 551, 455 cm^{-1}; MS (m/z): HRMS (ESI) Calcd. for $C_{66}H_{81}ClN_2O_{12}Na$ ($[M + Na]^+$): 1151.5376, found: 1151.5363.

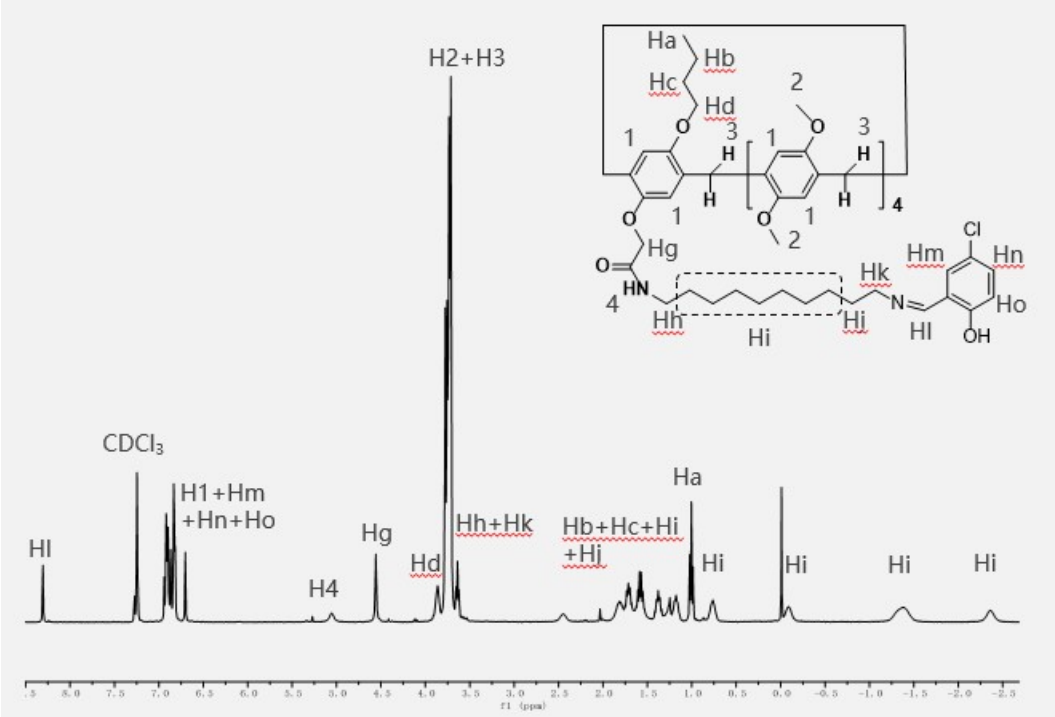


Figure S12. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293 K) of **2b**.

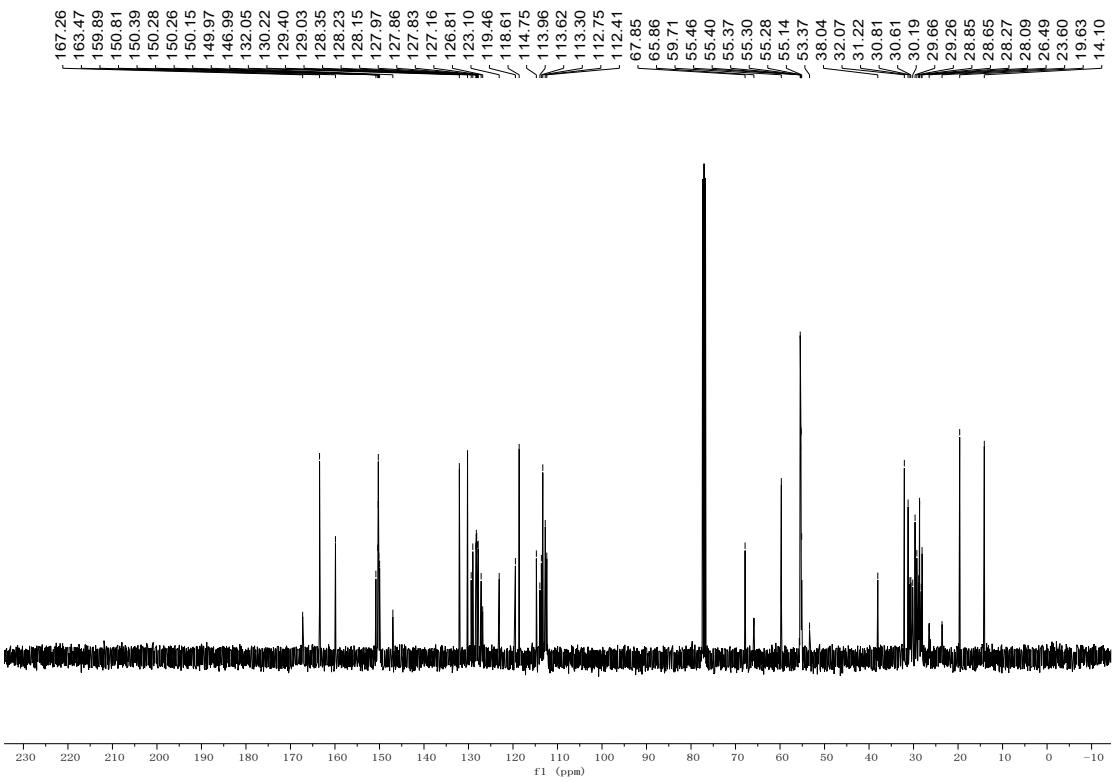


Figure S13. ^{13}C NMR spectrum ($CDCl_3$, room temperature, 100 MHz) of **2b**.

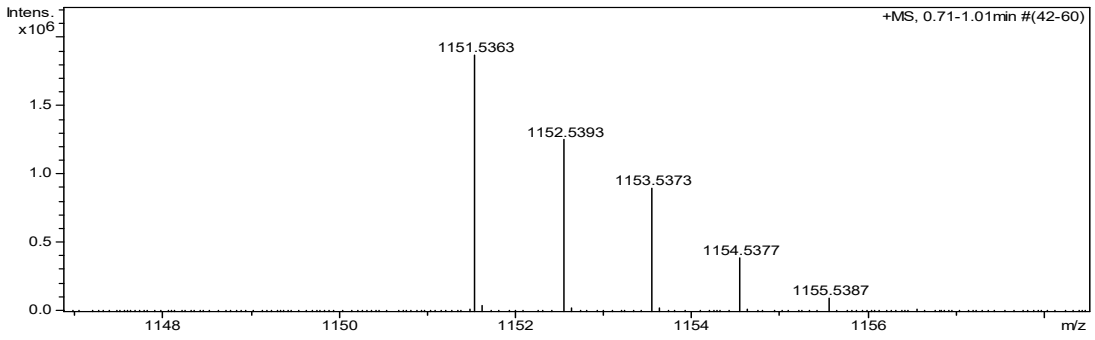


Figure S14 Mass spectra of **2a** Calcd. for $C_{66}H_{81}ClN_2O_{12}([M + Na]^+)$: 1151.5376, found: 1151.5363.

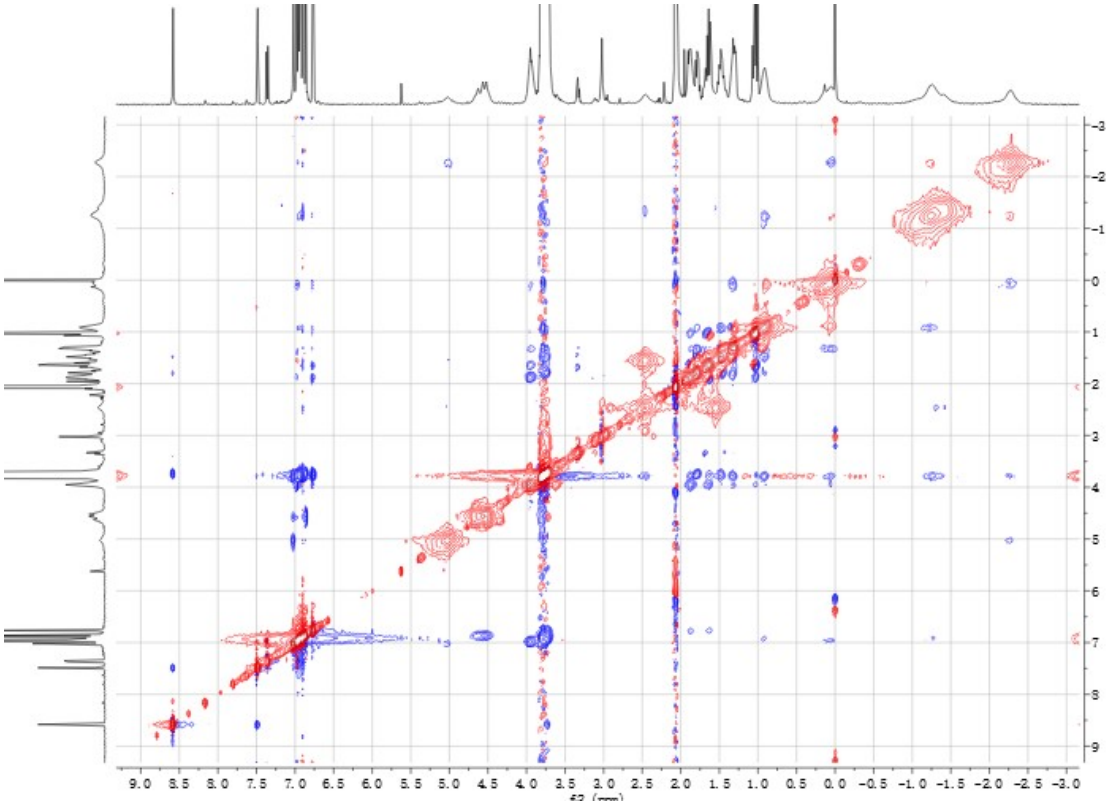


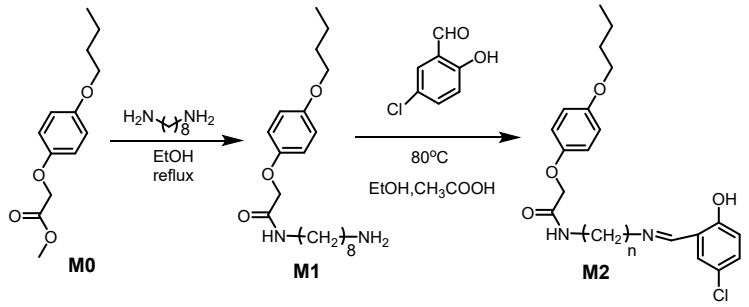
Figure S15. 2D NMR of **2b**.

Table S2 Information of crystal data for 2b

Phase	
Empirical formula	$C_{66}H_{81}ClN_2O_{12}$
Formula weight	1129.77
Temperature(K)	296(2)
Wavelength(Å)	0.71073
Crystal system,	Triclinic
space group	P-1
a(Å)	12.2666(11)
b(Å)	14.3343(12)
c(Å)	18.0514(17)
α(°)	77.570(3)
β(°)	89.492(3)
γ(°)	77.501(3)
Volume(Å^3)	3023.8(5)
Z	2
Calculated density(Mg·m^{-3})	1.241
Absorption coefficient(mm^{-1})	0.127
F(000)	1208
Crystal size(mm)	0.260 x 0.220 x 0.180
Theta range for data collection(°)	2.095 to 26.000
hkl ranges	-15 to 13, -17 to 17, -22 to 22
Reflections collected	42851 / 11871
unique	R(int)= 0.0699
Completeness to theta	99.6%
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	11871 / 138 / 740
Goodness-of-fit on F^2	1.014
Final R indices [I>2σ(I)]	R_1= 0.0937, wR_2= 0.2368
R indices (all data)	R_1= 0.1988, wR_2= 0.2989
Largest diff. peak and Hole(e·Å^3)	0.796 and -0.510

4. Synthesis of M2

Scheme S3. Synthetic route of **M2**



Synthesis of compound **M1**: **M0** (1 g, 4.2 mmol) and 1,8-octanediamine (6.463 g, 44.8 mmol) were added to 20 mL of anhydrous ethanol solution and reacted at 75°C for 12 hours. The organic solvent was removed by rotating under reduced pressure, and the compound **M1** was obtained by column chromatography (volume ratio: dichloromethane : methanol=10:1). White solid, 60%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (s, 4H, ArH), 5.30 (s, 1H, NH), 4.42 (s, 2H, CH_2), 3.91 (t, J = 6.5 Hz, 2H, CH_2), 3.36 – 3.29 (m, 2H, CH_2), 2.67 (t, J = 7.0 Hz, 2H, CH_2), 1.78 – 1.70 (m, 2H, CH_2), 1.57 – 1.39 (m, 10H, CH_2), 1.30 (s, 4H, CH_2), 0.97 (t, J = 7.4 Hz, 3H, CH_3).

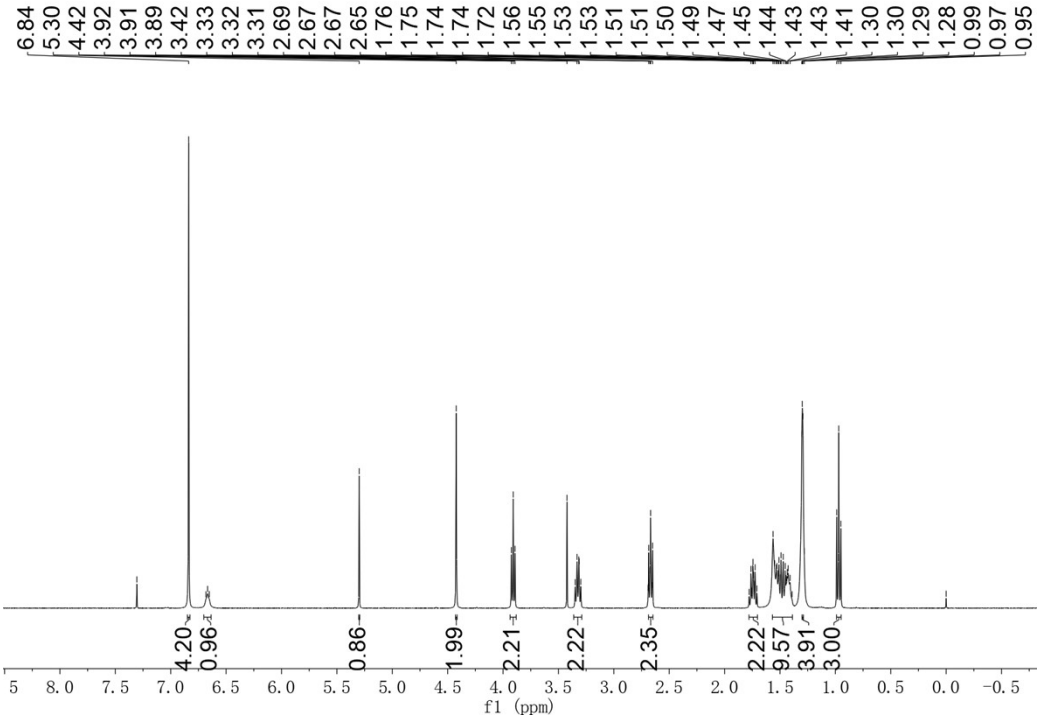


Figure S16. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293 K) of **M1**.

Synthesis of compound **M2**: **M1** (0.193 g, 0.55 mmol) and 5-chlorosalicylaldehyde (0.079 g, 0.5 mmol) were added to 20 mL of anhydrous ethanol solution and reacted at 80 °C for 4 hours. The organic solvent was removed by rotating under reduced pressure, and the compound **M2** was obtained by column chromatography (volume ratio: ethyl acetate: petroleum ether=1:5). Yellow solid, 50%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 13.64 (s, 1H, OH), 8.26 (s, 1H, CH), 7.25 – 7.20 (m, 1H, ArH), 6.89 (d, J = 8.6 Hz, 1H, ArH), 6.84 (s, 4H, ArH), 6.62 (d, J = 23.1 Hz, 1H, ArH), 4.43 (s, 2H, CH_2), 3.91 (t, J = 6.5 Hz, 2H, CH_2), 3.59 (t, J = 6.8 Hz, 2H, CH_2), 3.33 (m, 2H, CH_2), 1.72 (m, 4H, CH_2), 1.50 – 1.44 (m, 2H, CH_2), 1.30 (m, 10H, CH_2), 0.97 (t, J = 7.4 Hz, 3H, CH_3).

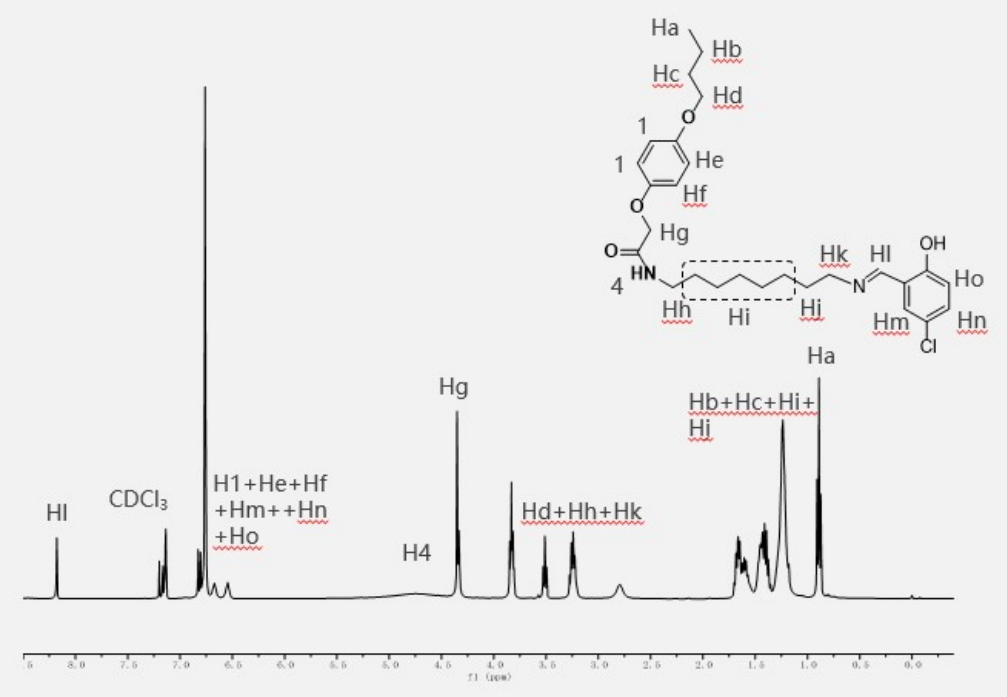


Figure S17. ^{1}H NMR spectrum ($CDCl_3$, room temperature, 100 MHz) of **M2**.

5. Synthesis of 2b-Zn

2b (0.226 g, 0.20 mmol) and 0.022g CH_3ONa were dissolved in 10 mL CH_3OH, then $Zn(CH_3COO)_2$ (0.018 g, 0.10 mmol) was added to the above solution, the mixture was reacted for 6 hours at room temperature. After the inorganic salts were removed by filtration, the organic solvent was collected and removed by rotating under reduced pressure, and the compound **2b-Zn** was obtained washing with CH_3OH and CH_3OCH_3.

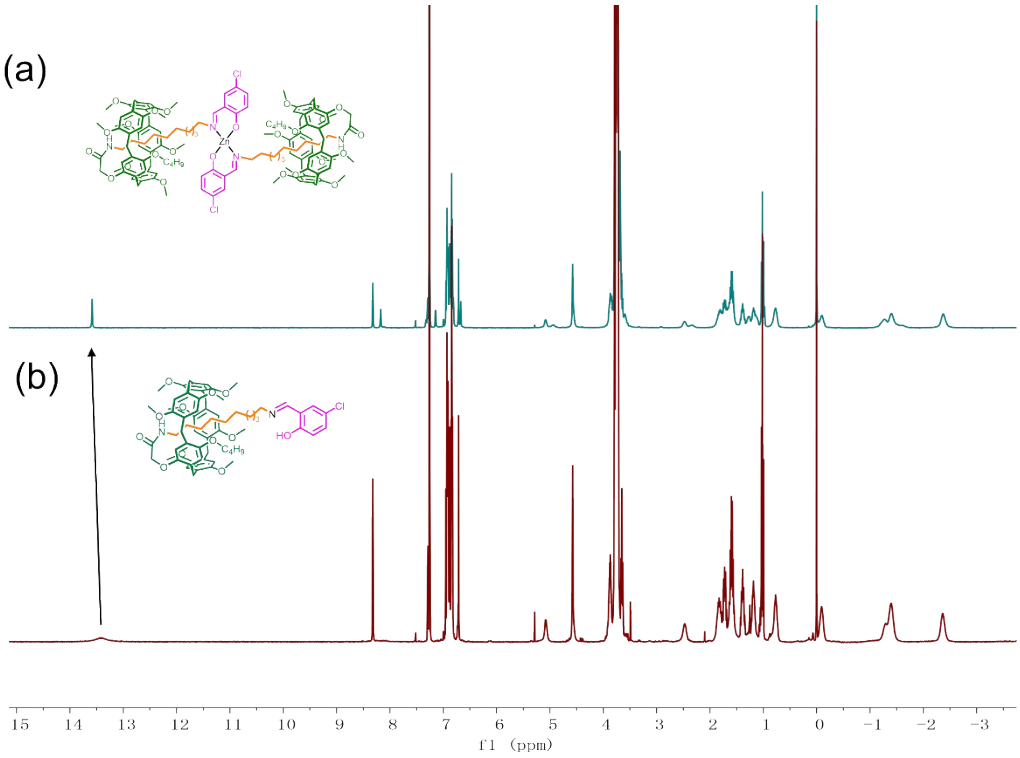


Figure S18. ^1H NMR spectra (400 MHz, $CDCl_3$/Acetonitrile-D_3, 298 K) of (a) **2b-Zn** and (b) **2b**.

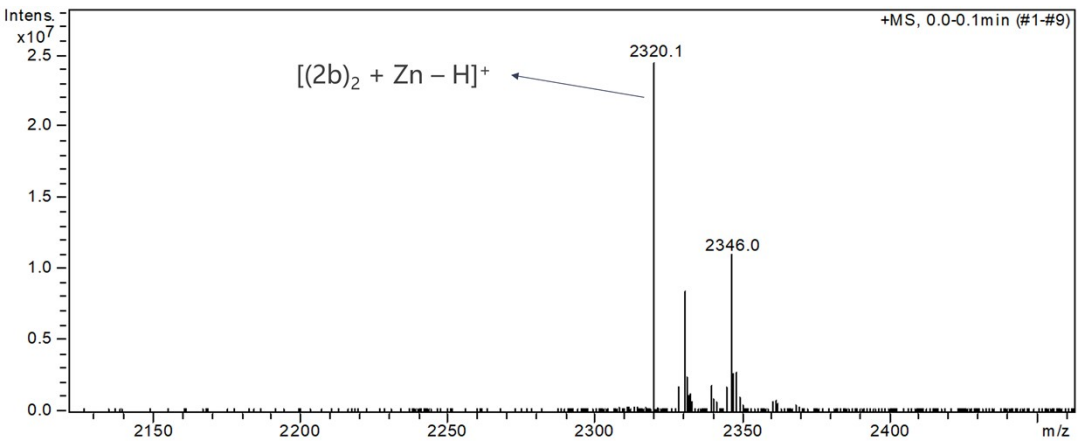


Figure S19. Mass spectra of complex, Calcd. for $C_{132}H_{161}Cl_2N_4O_{24}$ ([2 (**2b**) + Zn - H]$^+$):

2320.0, found: 2320.1.

6. Fluorescence investigation

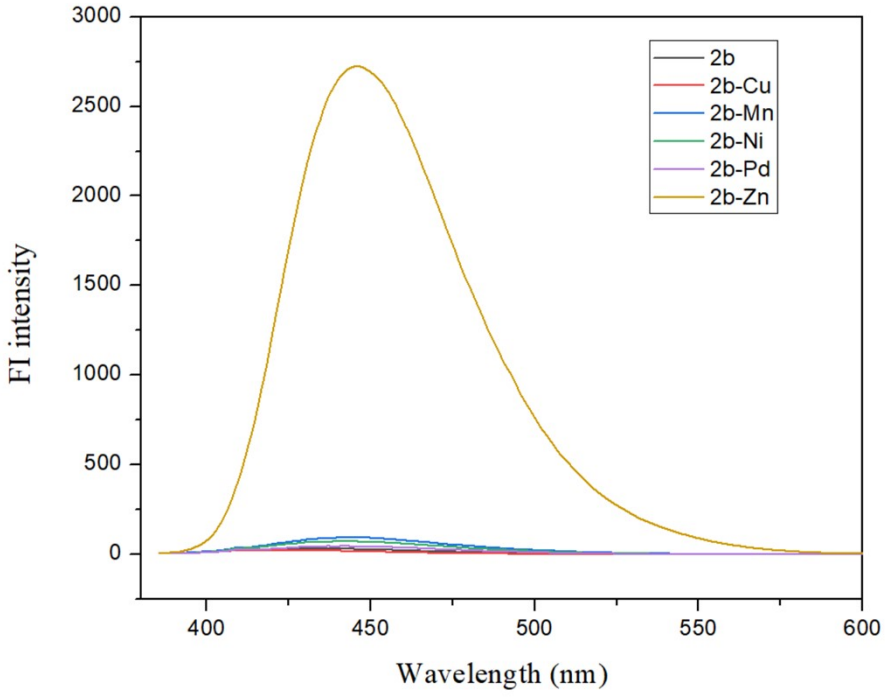


Figure S20. Fluorescence emission spectra of $CHCl_3$ solution of **2b** complex with different metal ions. ([C] = 10^{-5} M)

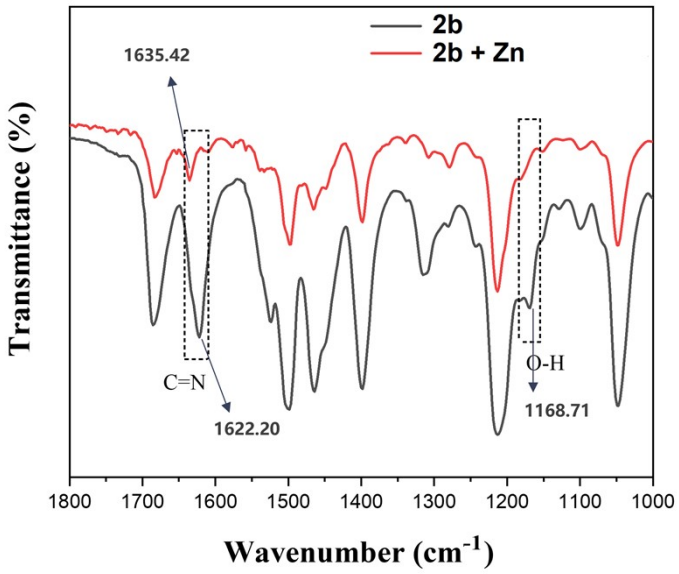


Figure S21 HR-IR spectra of **2b** and **2b**-Zn.

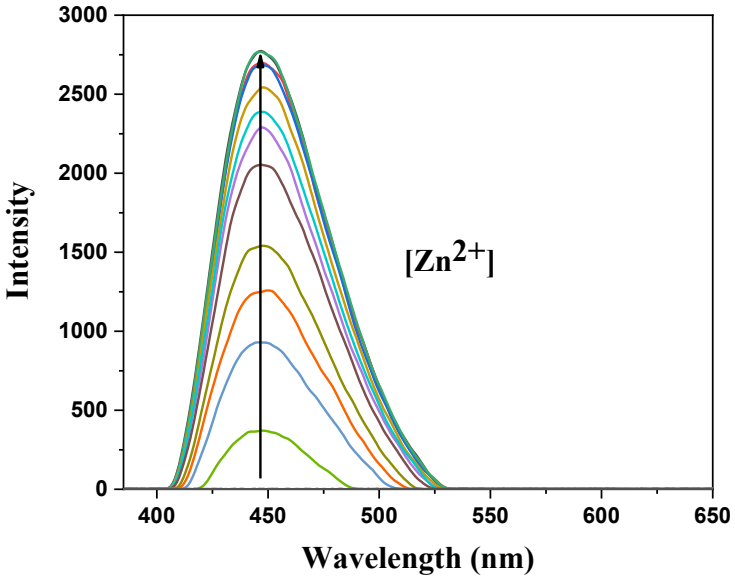


Fig. S22 Fluorescence titration spectra of **2b** with Zn^{2+}

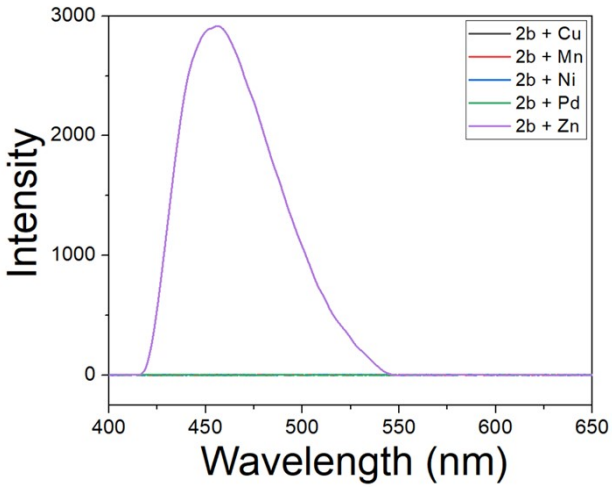


Fig. S23 Fluorescence emission spectra of thin solid films of 2b with different metal ions.

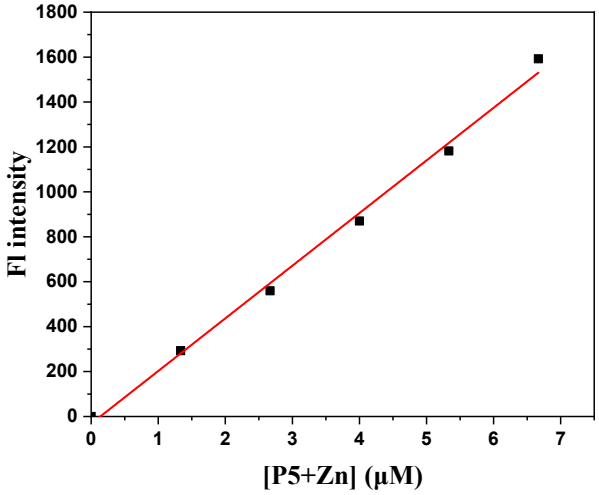


Fig. S24 The fluorescence intensity of **2b** against different concentration of Zn^{2+}.

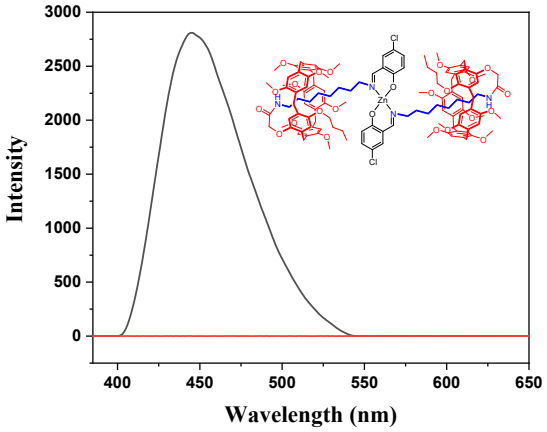


Figure S25. Fluorescence spectra of 2a@Zn (black line) and 2a (red line).

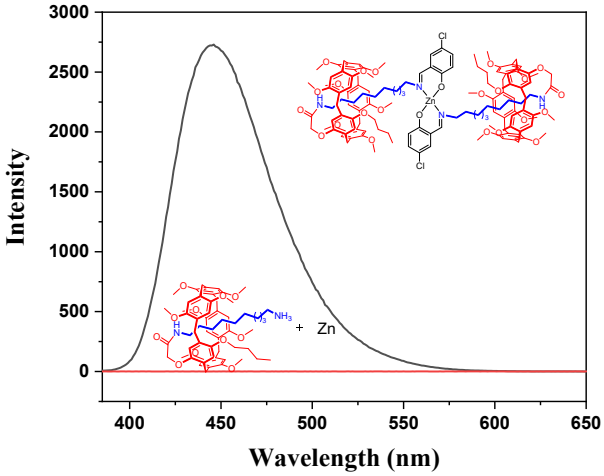


Figure S26 Fluorescence spectra of **2b**@Zn (black line) and **1b**@Zn (red line).

M1：^{13}C NMR (101 MHz, $CDCl_3$) δ 168.42, 154.23, 151.21, 115.59, 115.52, 115.48, 77.32, 68.22, 68.15, 42.17, 42.14, 38.98, 33.73, 33.70, 31.34, 29.50, 29.33, 29.19, 26.82, 26.77, 19.22, 13.86; MS (m/z): HRMS (ESI) Calcd. for $C_{20}H_{34}N_2O_3$([M+H]$^+$): 351.2648, found: 351.26288.

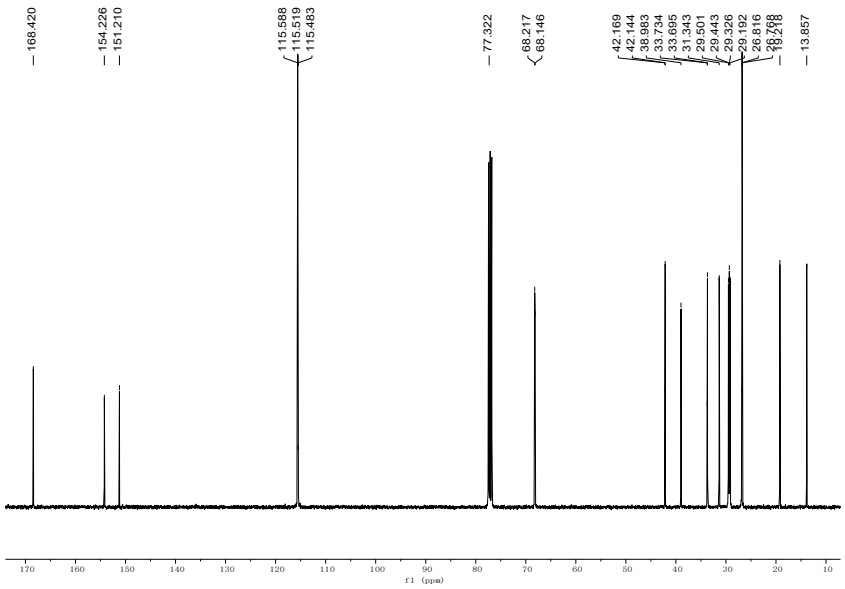


Fig. S27 ^{13}C NMR ($CDCl_3$, room temperature, 400 MHz) of M1.

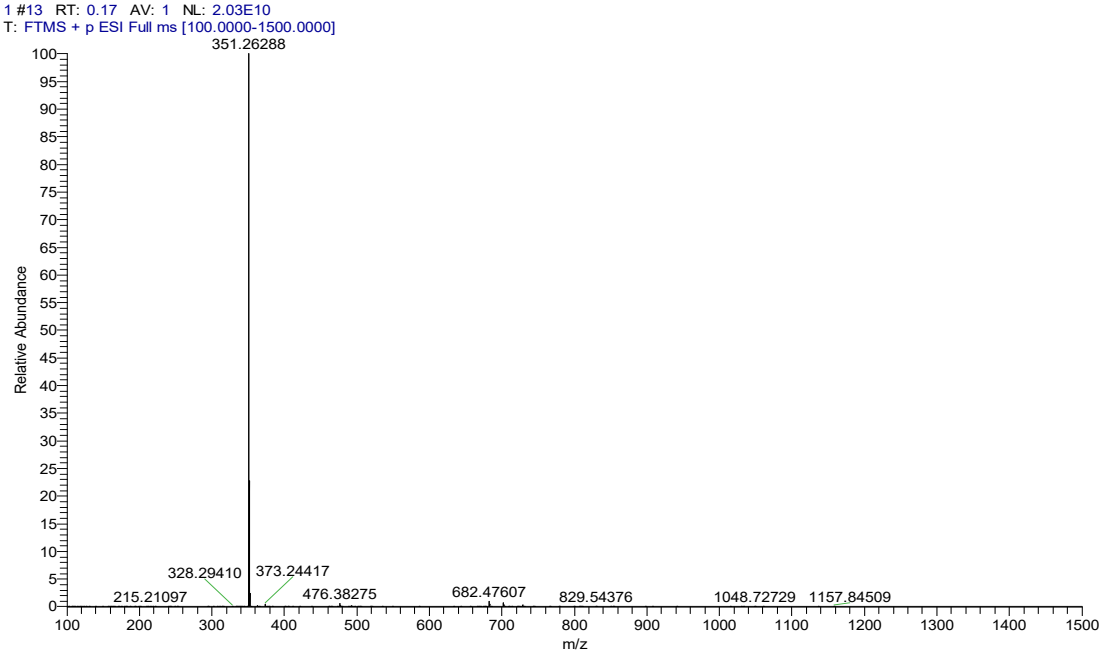


Fig. S28 MS spectrum of M1.

M2: ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.55, 168.43, 163.36, 160.05, 154.26, 151.22, 131.91, 130.21, 122.91, 119.47, 118.63, 115.66, 115.61, 115.51, 77.27, 68.25, 68.16, 68.13, 59.44, 40.39, 38.99, 38.96, 31.37, 30.68, 29.50, 29.15, 29.11, 28.94, 27.04, 26.76, 26.63, 26.49, 19.25, 13.88; MS (m/z): HRMS (ESI) Calcd. for $C_{27}H_{37}ClN_2O_4$([M+H]$^+$): 489.2520, found: 489.24997.

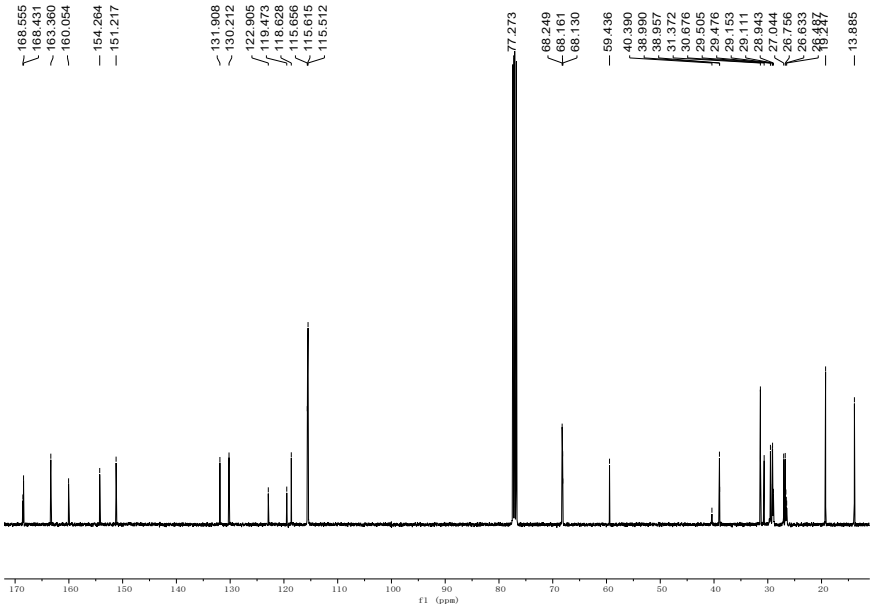


Fig. S29 ^{13}C NMR (101 MHz, $CDCl_3$) spectrum of M2.

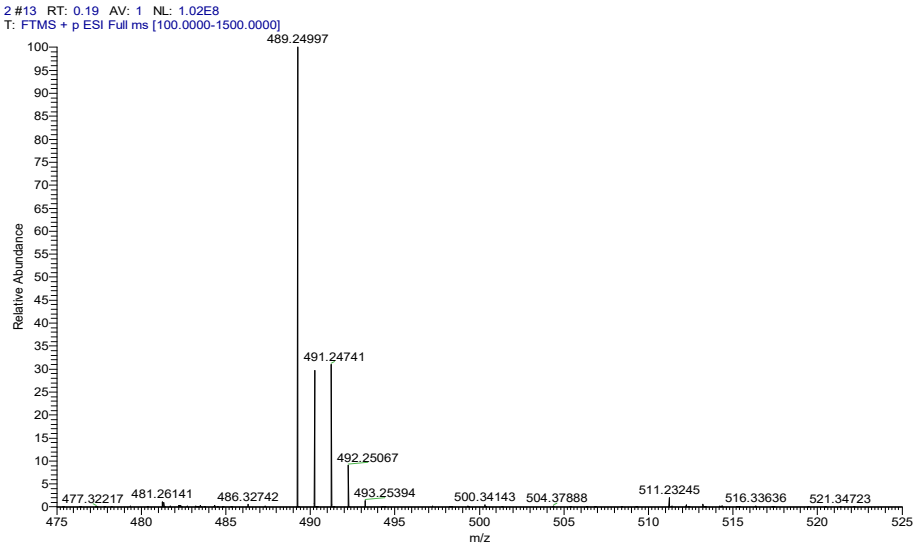


Fig. S30 MS spectrum of M2

References

S1. Runmiao Zhang, Chenwei Wang, Renhua Long, Tingting Chen, Chaoguo Yan, and Yong Yao, *Fron. Chem.*, **2019**, *7*, 508.

S2. Runmiao Zhang, Xin Yan, Hao Guo, Lanping Hu, Chaoguo Yan, Yang Wang, and Yong Yao, *Chem. Commun.*, **2020**, *56*, 948-951.