Supplementary Information

New Switchable [2]Pseudorotaxanes Formed by Pyridine N-oxide Derivatives with Diamide-based Macrocycles

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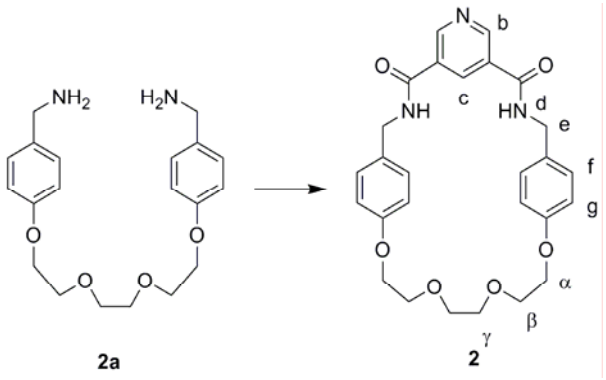
1. Experimental

General: Unless stated otherwise, all reagent and solvents were purchased from commercial sources. Anhydrous $CHCl_2/CH_3CN$ was obtained by distillation from CaH_2 under N_2. Anhydrous THF was obtained by distillation from Na/ph_2CO under N_2. Unless stated otherwise, all reactions were carried out under N_2 atmospheres. M.p.=melting point. Thin layer chromatography was performed on precoated silica gel plates. Column chromatography was carried out using silica as the stationary phase. All ^1H NMR and ^{13}C NMR were recorded on a Varian NMR system 400, at 295K. Chemical shifts are reported in parts per million (ppm). Coupling constants (J) are reported in hertz (Hz). Multiplicities are given as s(singlet), d(double), t(triplet), q(quartet), m(multiplet) and br(broad). Low-resolution electrospray ionization mass spectra were recorded with Thermo Finnigan LCQ Deca XP Max LC/MSn. High-resolution electrospray ionization mass spectra were recorded on Bruker Apex IV FTMS at Peking University. X-ray crystallographic was performed on Bruker SMART APEX II.

1.1. Sythesis of macrocycle 1 and 2

pyridine-3, 5-dicarbonyl chloride: A suspension of pyridine-3,5-dicarboxylic acid in thionyl dichloride was refluxed at 100°C for 6 hours, with exhaust gas treatment device. After the suspension became homogeneous, the solvent was removed under reduced pressure. The residue was used immediately without further purification.

Compound 1: Macrocycle **1** was synthesized by a literature procedure. [1] M.p.231.3-232.6°C; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.01 (s,1H), 7.94 (d, J = 7.8 Hz, 2H), 7.42 (t, J = 7.8 Hz,1H), 7.13 (d, J = 8.6 Hz, 4H), 7.01 (s, 2H), 6.68 (d, J = 8.6 Hz, 4H), 4.46 (d, J = 5.3 Hz, 4H), 4.01 – 3.89 (m, 4H), 3.88 – 3.75 (m, 4H), 3.70 (s, 8H); LR-MS (ESI): *m/z* calculated for $[\mathbf{1} + H]^+$ $C_{30}H_{35}N_2O_7$ 535.24, found 535.49 $[\mathbf{1} + H]^+$.



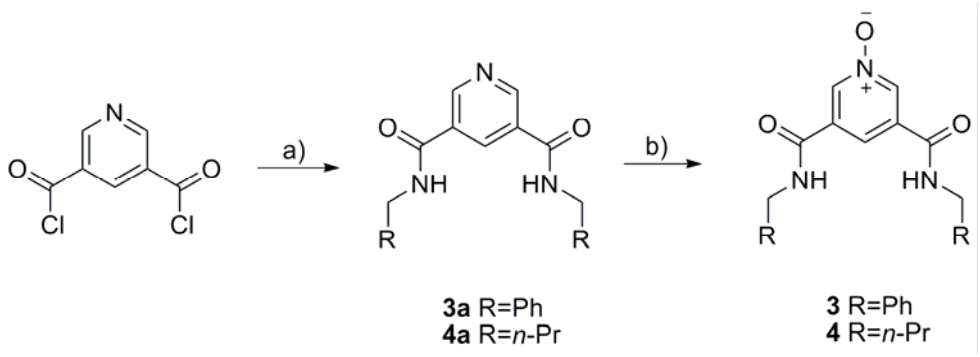
Scheme S1. Synthesis of macrocycle **2**. Reagents and conditions: pyridine-3, 5-dicarbonyl chloride, CH_2Cl_2, Et_3N, 0°C -r.t., 3 days, 28.6%.

2a: 2a was synthesized by a literature procedure. [1] M.p. 48.7-49.2 °C; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.20 (d,

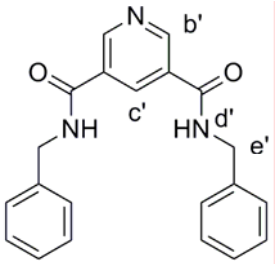
J = 8.0 Hz, 4H, Ar-H), 6.88 (d, *J* = 7.6 Hz, 4H, Ar-H), 4.12 (t, *J* = 4.8 Hz, 4H, benzyl-H), 3.86 (t, *J* = 4.7 Hz, 4H, α-OCH_2), 3.79 (s, 4H, β-OCH_2), 3.75 (s, 4H, γ-OCH_2); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 157.64, 135.62, 128.22, 114.63, 70.82, 69.77, 67.42, 45.82; LR-MS (ESI): m/z calculated for [**2a** + Na]$^+$ $C_{20}H_{28}N_2O_4Na$ 383.19, found 383.37 [**2a** + Na]$^+$.

Compound 2: To a solution of **2a** (0.97g, 2.7mmol) and NEt_3 (2.3ml) in CH_2Cl_2 100ml was added dropwise a solution of pyridine-3, 5-dicarbonyl chloride (3 mmol) in CH_2Cl_2 (20ml) over a period of 3 days at 0°C. After the solvent was removed under reduced pressure, the crude residue was purified by column chromatography (chloroform: acetone=8:5) to yield the product as a colorless powder (0.38g, 28.6%). M.p.241.1-244.0°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.96 (s, 2H, Hb), 8.74 (t, *J* = 5.1 Hz, 2H, Hd), 8.25 (s, 1H, Hc), 7.22 (d, *J* = 8.3 Hz, 4H, Hf), 6.84 (d, *J* = 8.3 Hz, 4H, Hg), 4.33 (d, *J* = 5.1 Hz, 4H, He), 4.05 (d, *J* = 4.3 Hz, 4H, α-OCH_2), 3.72 – 3.61 (m, 4H, β-OCH_2), 3.51 (s, 4H, γ-OCH_2); ^{13}C NMR (101 MHz, DMSO-d_6) δ = 165.05, 158.13, 150.92, 130.97, 130.26, 114.84, 70.41, 69.18, 67.60, 43.24. LR-MS (ESI): *m/z* calculated for [**2** + H]$^+$ $C_{27}H_{30}N_3O_6$ 491.2135, found 492.66 [**2** + H]$^+$, 983.48 [$\mathbf{2}_2$ + H]$^+$, 1005.27 [$\mathbf{2}_2$ + Na]$^+$, 1497.09 [$\mathbf{2}_3$ + H]$^+$; HR-MS (ESI), found 492.2126 [**2** + H]$^+$, 983.4167[$\mathbf{2}_2$ + H]$^+$, 1474.6237 [$\mathbf{2}_3$ + H]$^+$.

1.2. Synthesis of pyridine N-oxides

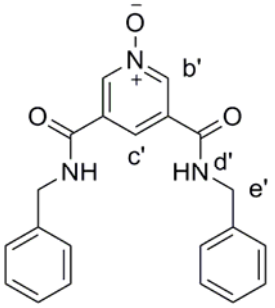


Scheme S2. Synthesis of the guest compound pyridine N-oxide. Reagents and conditions: a) **3a**, benzyl amine,**4a**, *n*-butylamine, CH_2Cl_2, Et_3N, 0°C-r.t., overnight,**3a**,82.0%,**4a**,86.9%. b) m-Chloroperbenzoic acid, $CHCl_3$, 0°C-r.t.,3 days, **3**, 56.2%, **4**, 54.6%.



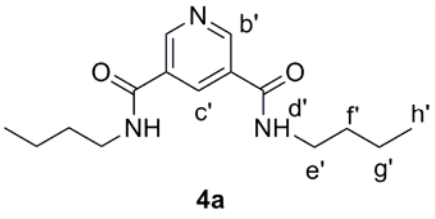
3a

Compound 3a: To a solution of pyridine-3, 5-dicarbonyl chloride (6mmol) and NEt_3 (4.2ml) in CH_2Cl_2 (20ml) at 0°C was added benzyl amine (30mmol), and stirred overnight. The solvent was removed under reduced pressure and the crude residue was purified by column chromatography (chloroform: acetone=8:5) to give a colorless solid as product (1.70g, 82.0%). M.p. 194.3-196.1°C; ^{1}H NMR (400 MHz, $CDCl_3/CD_3OD$=3:1) δ = 9.09 (s, 2H, Hb'), 8.57 (s, 1H, Hc'), 7.39 – 7.30 (m, 10H, Ar-H), 7.30 – 7.24 (m, 2H, Hd'), 4.61 (d, J = 1.3 Hz, 4H, He'); ^{13}C NMR (101 MHz, $CDCl_3/CD_3OD$=3:1) δ = 165.29, 150.48, 137.88, 134.37, 130.15, 128.68, 127.81, 127.55, 44.14, 44.01; LR-MS (ESI): *m/z* calculated for [**3a**+H]$^+$ $C_{21}H_{20}N_3O_2$ 346.16, found 346.81 [**3a**+H]$^+$.



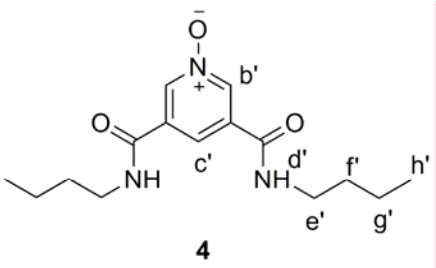
3

Compound 3: To a solution of **3a** (3.5mmol) in $CHCl_3$ (18ml) at ice bath was added m-chloroperoxybenzoic acid (10.5mmol) carefully. The solution was stirred at room temperature for 3 days. Then cold water was added, followed by 10% Na_2CO_3 aqueous solution. The orange oil was separated and dried over $MgSO_4$, evaporated to give a crude material, which was purified by column chromatography (chloroform: acetone=8:5) to give a colorless solid as product (0.71g, 56.2%). M.p.246.9-247.3°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.42 (t, J = 5.6 Hz, 2H, Hd'), 8.74 (t, J = 1.4 Hz, 2H, Hb'), 8.21 (d, J = 1.4 Hz, 1H, Hc'), 7.51 – 7.07 (m, 10H, Ar-H), 4.49 (d, J = 5.6 Hz, 4H, He'); ^{13}C NMR (101 MHz, DMSO-d_6) δ = 162.11, 139.44, 138.74, 133.24, 128.39, 127.45, 127.03, 122.88, 42.94; LR-MS(ESI):*m/z* calculated for [**3** + H]$^+$ $C_{21}H_{20}N_3O_3$ 362.1505,found 362.55 [**3** + H]$^+$, 754.53 [$\mathbf{3}_2$ + Na]$^+$, 1106.27 [$\mathbf{3}_3$ + Na]$^+$; HR-MS (ESI), found 362.1495 [**3** + H]$^+$, 723.2911 [$\mathbf{3}_2$ + H]$^+$, 1084.4334 [$\mathbf{3}_3$ + H]$^+$, 1445.5786 [$\mathbf{3}_4$ + H]$^+$, 1828.7018 [$\mathbf{3}_5$ + H]$^+$.



4a

Compound 4a: Compound **4a** was synthesized from pyridine -3, 5-dicarbonyl chloride and *n*-butylamine as described for **3a**, purified by column chromatography (dichloromethane: ether=3:2) to yield the desired product (86.9%). M.p.169.5-170.2°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.08 (s, 2H, Hb'), 8.45 (s, 1H, Hc'), 6.82-6.55 (m, 2H, Hd'), 3.49 (dd, J = 13.4, 6.6 Hz, 4H, He'), 1.63 (dt, J = 14.9, 7.5 Hz, 4H, Hf'), 1.49 – 1.36 (m, 4H, Hg'), 0.97 (t, J = 7.3 Hz, 6H, Hh'); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 165.07, 150.51, 133.60, 130.34, 40.30, 31.78, 20.36, 13.97; LR-MS (ESI): *m/z* calculated for [**4a** + H]$^{+}C_{15}H_{24}N_3O_2$ 277.12, found 278.36 [**4a** + H]$^{+}$, 555.28 [$\mathbf{4a}_2$ + H]$^{+}$, 557.31 [$\mathbf{4a}_2$ + Na]$^{+}$, 854.17 [$\mathbf{4a}_3$ + Na]$^{+}$.



4

Compound 4: Compound **4** was synthesized from **4a** as described for **3**, and purified by column chromatography (dichloromethane: acetone=8:5) (54.6%). M.p.193.6-194.7°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.92 (s, 2H,Hb'), 8.23 (s, 1H, Hc'), 7.71 (br, 2H, Hd'), 3.46 (dd, J = 13.1, 6.7 Hz, 4H,He'), 1.68 – 1.58 (m, 4H,Hf'), 1.41 (dt, J = 14.2, 7.3 Hz, 4H,Hg'), 0.97 (t, J = 7.3 Hz, 6H,Hh'); ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.41, 140.32, 134.37, 40.60, 31.55, 20.39, 13.97; LR-MS(ESI): *m/z* calculated for [**4** + H]$^{+}$ $C_{15}H_{24}N_3O_3$ 293.17, found 294.44 [**4** + H]$^{+}$, 609.25 [$\mathbf{4}_2$ + Na]$^{+}$, 902.13 [$\mathbf{4}_3$ + Na]$^{+}$;HR-MS (ESI), found 294.1813 [**4** + H]$^{+}$, 609.3375, [$\mathbf{4}_2$ + Na]$^{+}$,902.5120 [$\mathbf{4}_3$ + Na]$^{+}$,1195.6854 [$\mathbf{4}_4$ + Na]$^{+}$, 1488.8643 [$\mathbf{4}_5$ + Na]$^{+}$.

2. ^{1}H NMR spectra of an equimolar solution of 1 and 3, 1 and 4, 2 and 3, 2 and 4

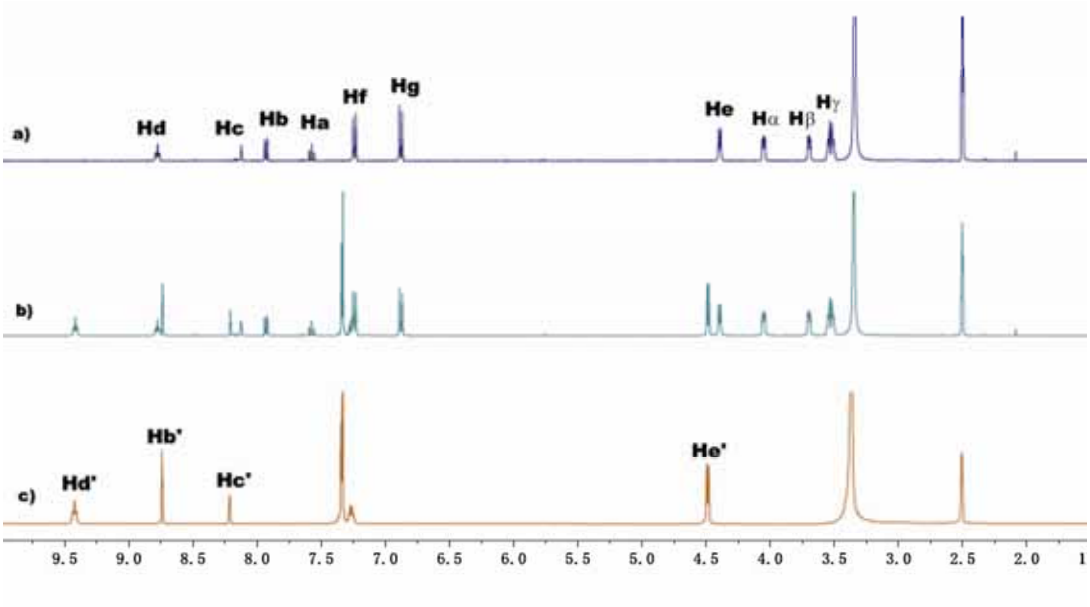


Figure S1. ^{1}H NMR spectra of a) macrocycle **1** (4mM)**,** b) an equimolar solution of **1** and **3,** and c) **3** (400MHz, DMSO-d_6, 295K).

The ^{1}H NMR spectra of an equimolar mixture of **1** and **3** in DMSO-*d*6 at 295K show no significant changes in the chemical shifts (Figure S1, b) as compared to that of the individual **1** and **3** in the same solvent, indicating that the hydrogen bonding between of **1** and **3** may not occur and the complex is not formed in the polar aprotic solvent DMSO.

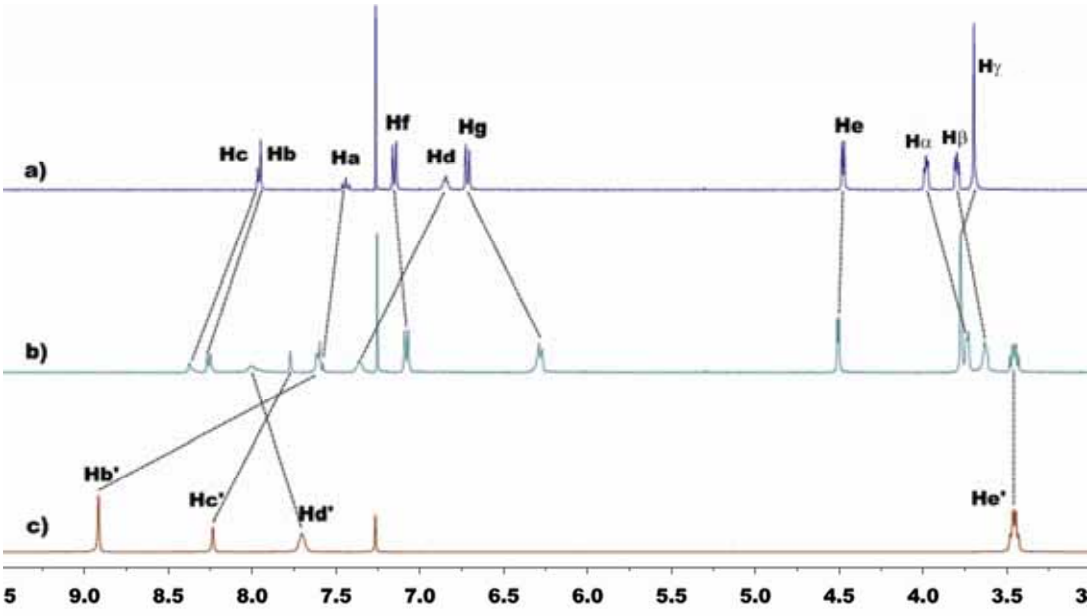


Figure S2. Partial ^{1}H NMR spectra of a) macrocycle **1** (4mM)**,** b) an equimolar solution of **1** and **4,** and c) **4** (400MHz, $CDCl_3$, 295K).

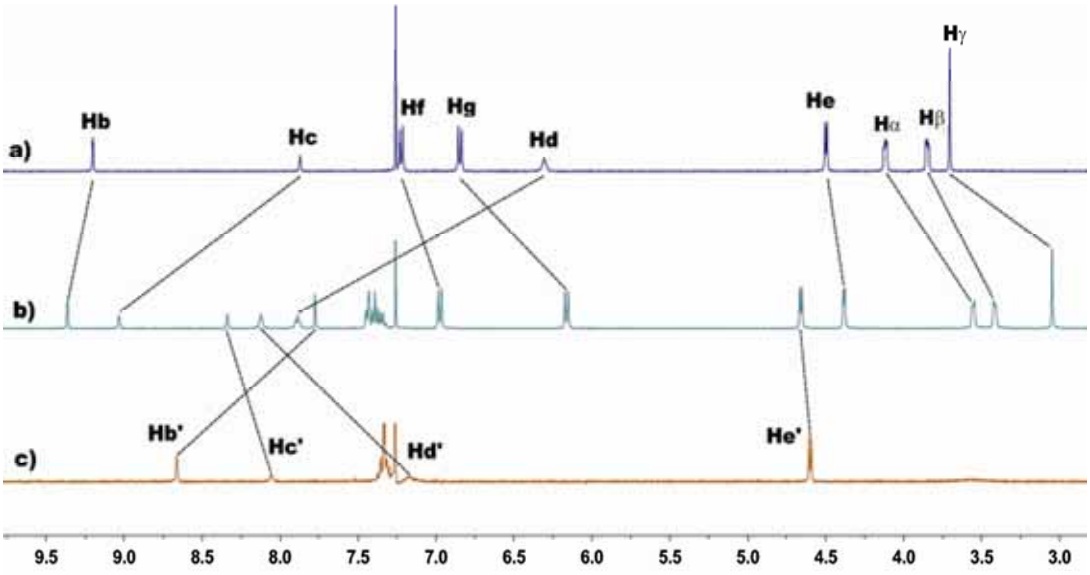


Figure S3. Partial ^{1}H NMRspectra of a) macrocycle **2** (4mM)**,** b) an equimolar solution of **2** and **3,** and c) **3** (400MHz, $CDCl_3$, 295K).

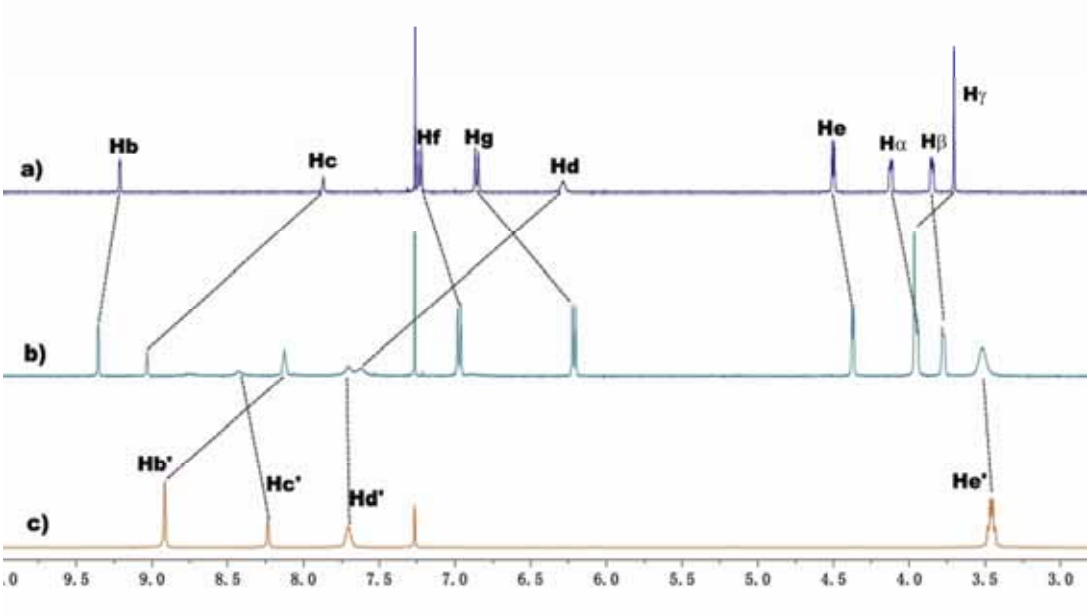


Figure S4. Partial ^{1}H NMR spectra of a) macrocycle **2** (4mM)**,** b) an equimolar solution of **2** and **4**, and c) **4** (400MHz, $CDCl_3$, 295K).

3. Association constants determination

^{1}H NMR titration was used for deterination of the association constant at 295K. Solutions were made in $CD_3OD/CDCl_3$ (V: V=1:3); the concentration of guest (pyridine N-oxides) was varied while the concentration of host (macrocycles) was held constant at 1.0×10^{-2} M. The association constant, K_a, was determined by observing the change in the chemical shift for the proton H_g of the host. Based on these NMR data, Δ_0, the difference in δ values for proton H_g of host in the uncomplexed and fully complexed species, was calculated by using the Benesi–Hildebrand method [2]. Then K_a was calculated from $1/\Delta = 1/(\Delta_0 K_a[G]_0) + 1/\Delta_0$. Usually $[G]_0$, the total initial concentration of guest, is used as an estimate of the concentration of uncomplexed guest, [G]. The intercepts of these plots give estimates of Δ_0 and from the slope K_a can be calculated. We used this Δ_0 value to produce a refined estimate of [G], since $[G] = [G]_0-(\Delta/\Delta_0)[H]_0$. Replotting the data using the new estimate of [G] provided improved estimates of Δ_0 and K_a. The process was repeated until constancy of these two parameters was achieved[3].

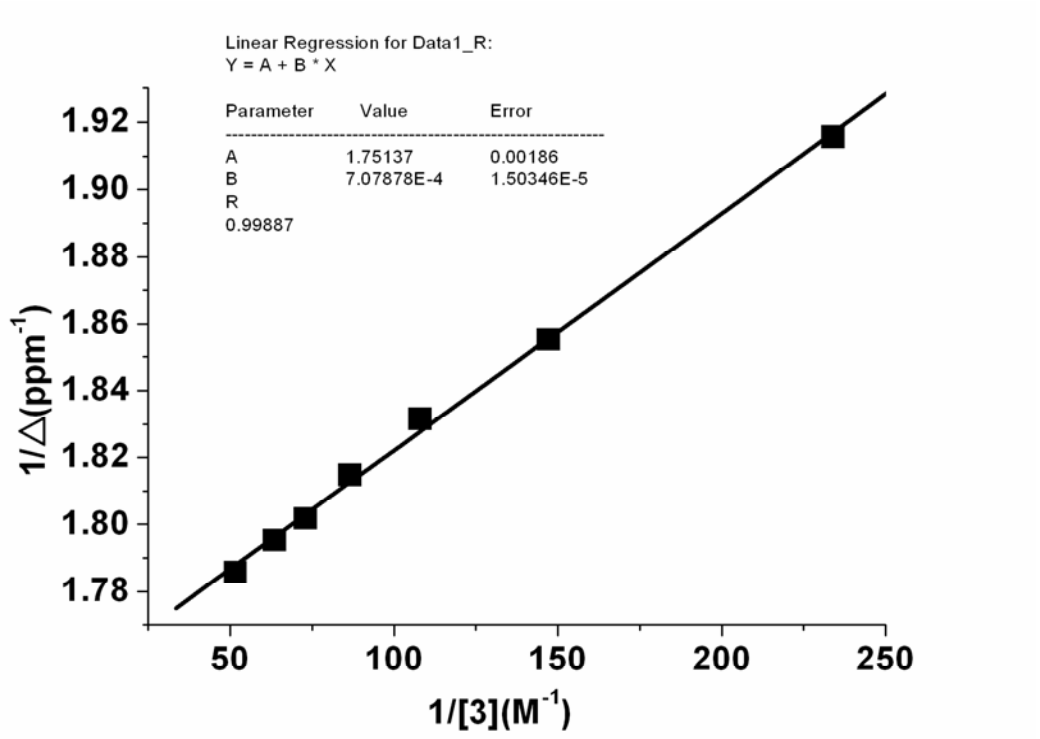


Figure S5. Benesi-Hildebrand plots for the formation of complex **1•3**: macrocycle **1** (10mM) with **3** in $CD_3OD/CDCl_3$ (V: V=1:3) at 295K.

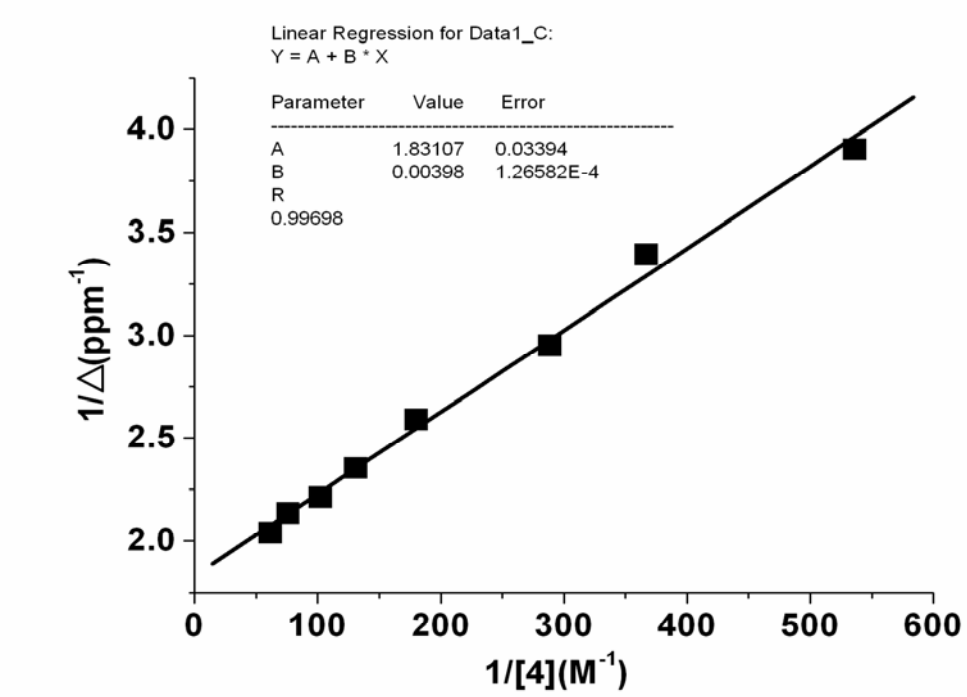


Figure S6. Benesi-Hildebrand plots for the formation of complex **1•4**: macrocycle **1** (10mM) with **4** in $CD_3OD/CDCl_3$ (V: V=1:3) at 295K

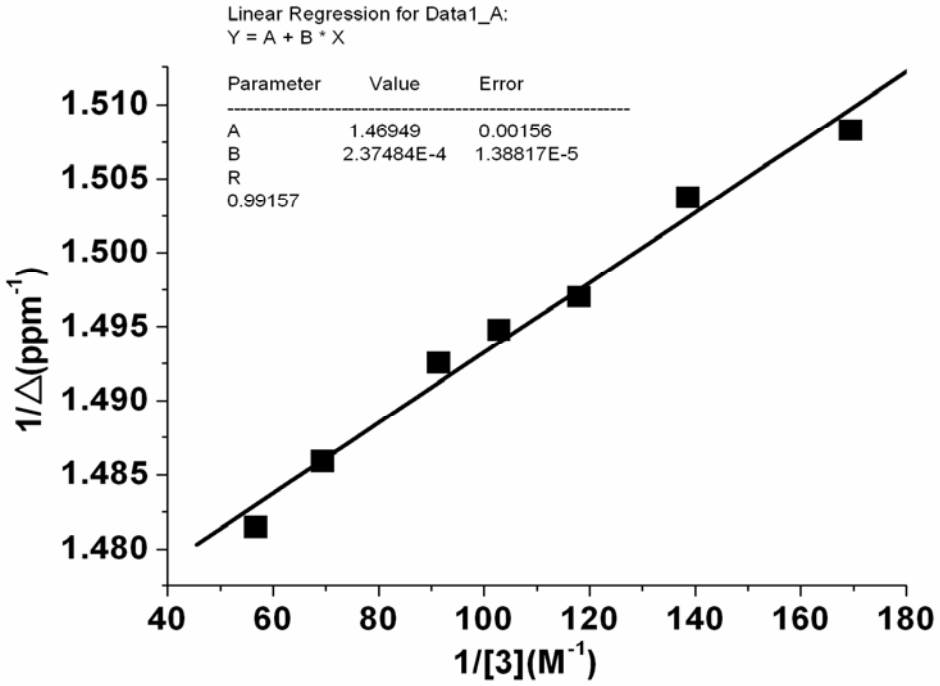


Figure S7. Benesi-Hildebrand plots for the formation of complex **2•3**: macrocycle **2**(10mM) with **3** in $CD_3OD/CDCl_3$ (V: V=1:3) at 295K.

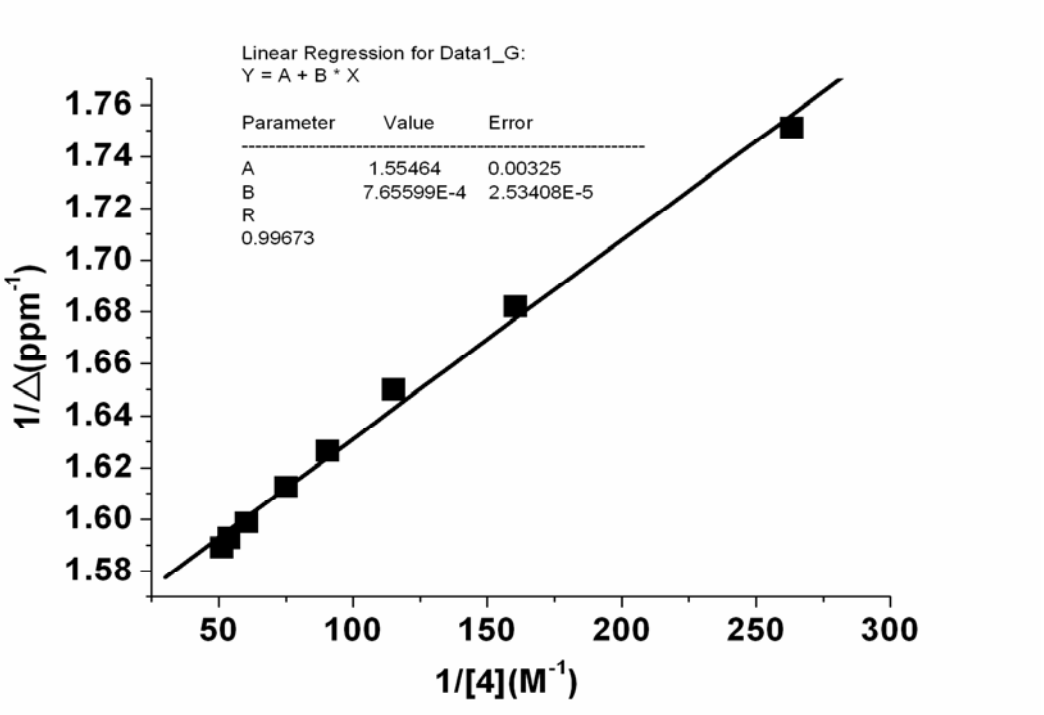


Figure S8. Benesi-Hildebrand plots for the formation of complex **2•4**: macrocycle **2** (10mM) with **4** in $CD_3OD/CDCl_3$ (V: V=1:3) at 295K

Table S1. Association constants (*K*a) for the complexes **1·3, 1·4, 2·3, 2·4** in $CD_3OD/CDCl_3$ (V: V=1:3) at 295K

Complex	*K*a(M^{-1})
1·3	$(2.2\pm0.6)\times10^3$
1·4	$(3.8\pm1.1)\times10^2$
2·3	$(5.5\pm0.4)\times10^3$
2·4	$(1.8\pm0.2)\times10^3$

4.Acid–base control process of pyridine N-oxide-based molecular switches

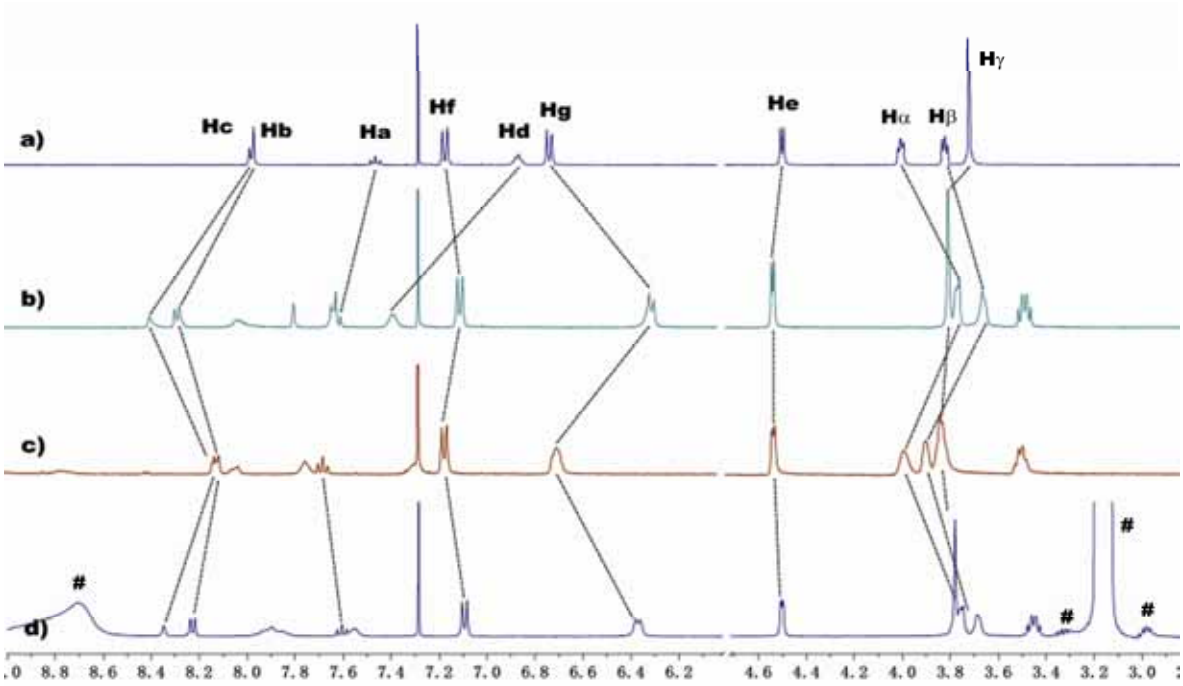


Figure S9. Partial ^{1}H NMR spectra of a) macrocycle **1**(4mM), b) an equimolar mixture of **1** and **4**(4mM), c) the mixture obtained after adding 40-fold molar excess of TFA to the solution in b),and d) the mixture obtained after adding 45-fold molar excess of TEA to the solution in c).
#:signal from solvent

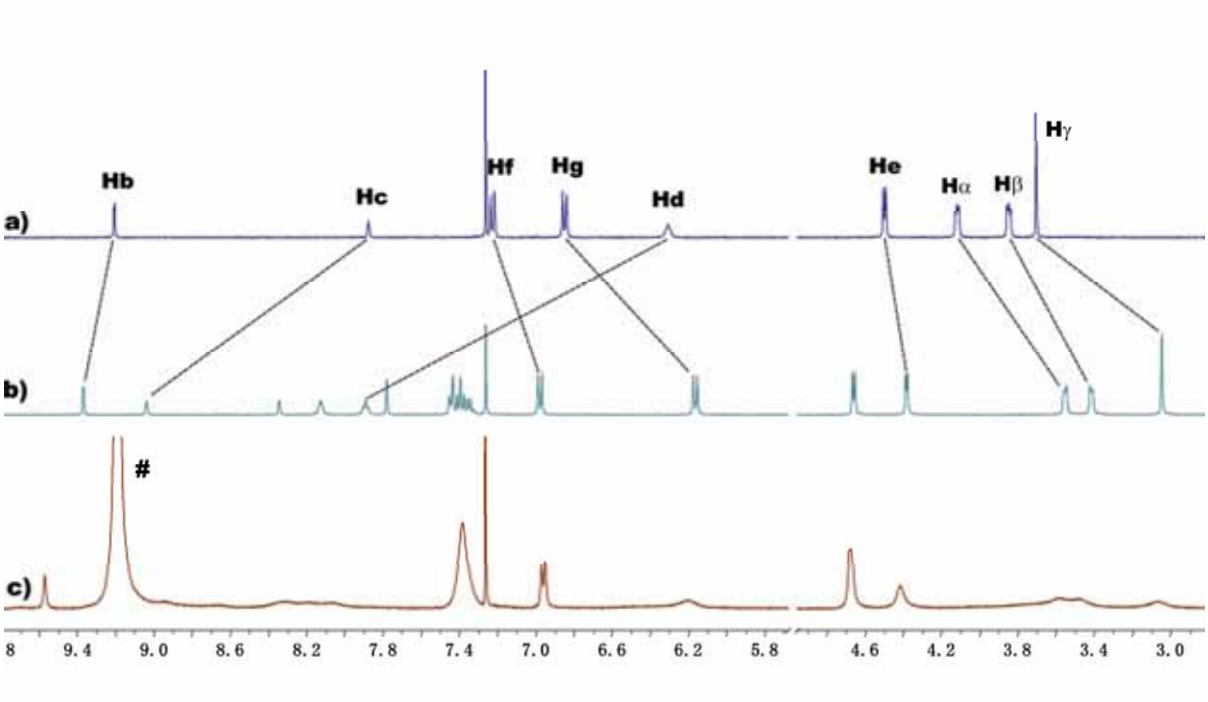


Figure S10. Partial ^{1}H NMR spectra of a) macrocycle **2** (4mM), b) an equimolar mixture of **2** and **3**(4mM), c) the mixture obtained after adding 90-fold molar excess of TFA to the solution in b).
#:signal from solvent

When an excess of trifluoroacetic acid (TFA) was added to the equimolar solution of **2** and **3** in $CDCl_3$, the ^{1}H NMR spectrum (**Figure S10, c**) of the resulting mixture showed almost no changes, indicating that the decomplexation of **2**·**3** did not occur upon addition of TFA.

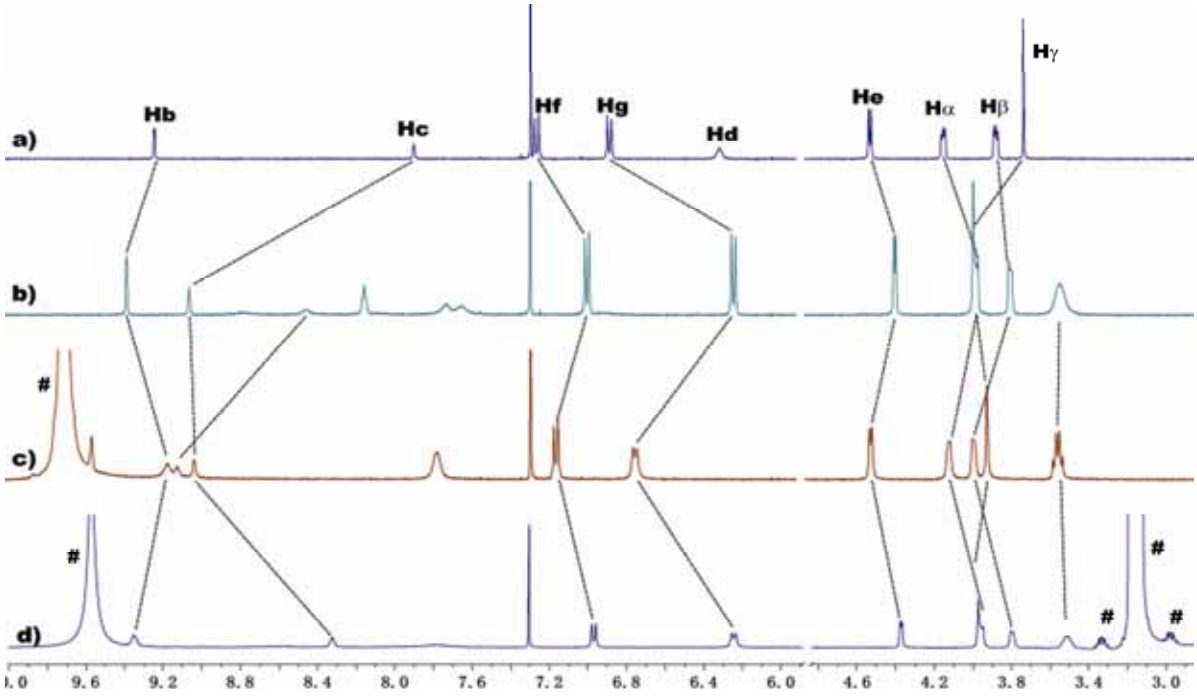


Figure S11. Partial ^{1}H NMR spectra of a) macrocycle **2**(4mM)**,** b) an equimolar mixture of **2** and **4** (4mM)**,** c) the mixture obtained after adding 60-fold molar excess of TFA to the solution in b), and d) the mixture obtained after adding 65-fold molar excess of TEA to the solution in c).
#:signal from solvent

5. X-ray structure of macrocycle 2, pseudorotaxane 1·3, 2·3

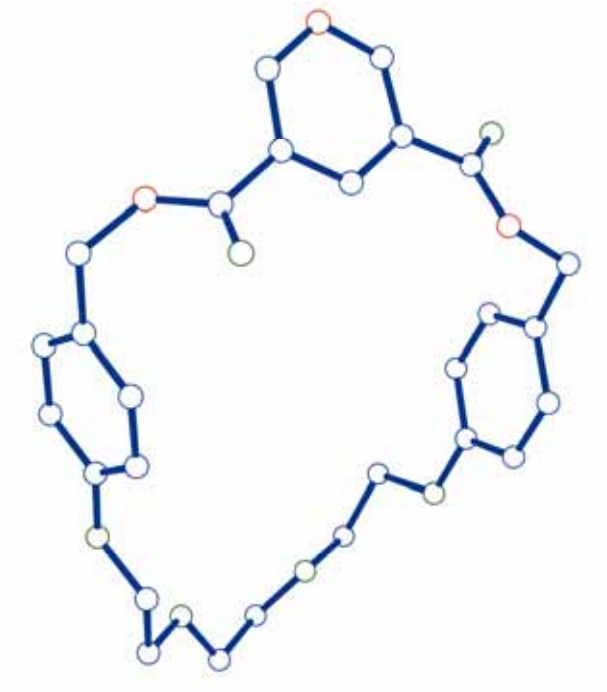


***Figure S12*.** Ball-stick views of the X-ray structure of macrocycle **2**. Carbon is blue, oxygens are green, and nitrogen is red. All hydrogen atoms have been omitted for clarity.

X-ray analysis data of macrocycle 2: Crystallographic data: block, colorless, 0.24×0.22×0.21 mm^3, $C_{27}H_{29}N_3O_6$, FW 491.53, Monoclinic, space group $P2_1/c$, a= 12.3749(14), b = 21.444(2), c = 9.7237(11) Å, α = 90.00, β = 93.946(2), γ = 90.00° , V = 2574.2(5) $Å^3$, Z = 4, D_c = 1.268 $g·cm^{-3}$, T = 298(2) K, μ = 0.090 mm^{-1}, 13253 measured reflections, 4635 independent reflections, 325 parameters, 0 restraints, $F(000)$ = 1040, R_1 = 0.0897, wR_2 = 0.1223(all data), R_1 = 0.0465, wR_2 = 0.1024 [$I > 2\sigma(I)$], R(int) = 0.0382, max. residual density 0.219 $e·Å^{-3}$, goodness-of-fit (F^2) = 1.027. CCDC No. 762537.

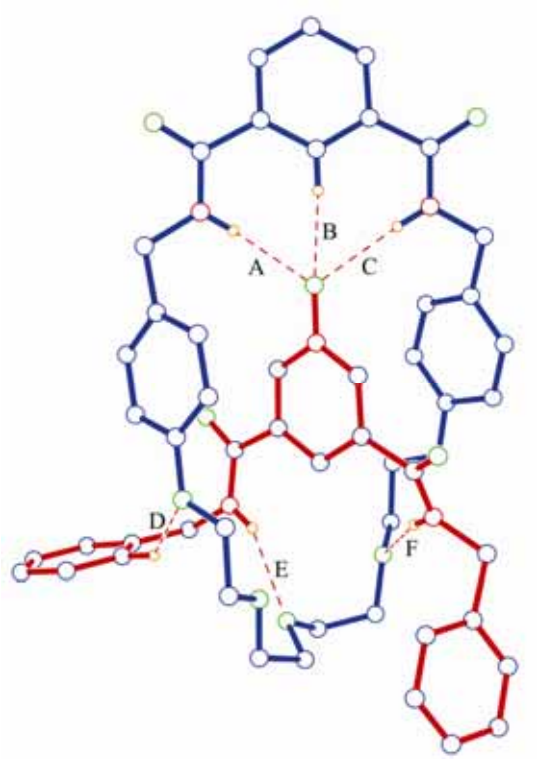


Figure S13. Ball-stick views of the X-ray structure of complex **1·3**. Macrocycle **1** is blue, pyridine N-oxide **3** is red, hydrogens are orange, oxygens are green, and nitrogen is red. Hydrogens except that involved in hydrogen bonding have been omitted for clarity.

Hydrogen-bond parameters: A): the distance of H···O is 2.214Å, the angle of N-H···O is 172.41 º, and the distance of N···O is 3.069Å. B): the distance of H···O is 2.196Å, the angle of C-H···O is 156.46 º, and the distance of C···O is 3.071Å. C): the distance of H···O is 2.272Å, the angle of C-H···O is 176.22 º, and the distance of C···O is 3.131Å. D): the distance of H···O is 2.524Å, the angle of C-H···O is 136.84 º, and the distance of C···O is 3.264Å. E): the distance of H···O is 2.307Å, the angle of N-H···O is 139.14 º, and the distance of N···O is 3.011Å. F): the distance of H···O is 2.606Å, the angle of N-H···O is 166.42 º, and the distance of N···O is 3.448Å.

X-ray analysis data of complex 1·3: Crystallographic data: block, colorless, 0.36×0.25×0.12 mm^3, $C_{51}H_{53}N_5O_{10}$, FW 895.98, Triclinic, space group P-1, a= 13.307(4), b = 13.970(2), c = 14.302(2) Å, α = 111.192(2), β = 103.103(3), γ = 101.085(3)° , V = 2301.7(9) $Å^3$, Z = 2, D_c = 1.293 $g{\cdot}cm^{-3}$, T = 298(2) K, μ = 0.091 mm^{-1}, 11963 measured reflections, 8284 independent reflections, 595 parameters, 0 restraints, F(000) = 948, R_1 = 0.1022, wR_2 = 0.1826(all data), R_1 = 0.0627, wR_2 = 0.1515 [$I > 2\sigma(I)$], R(int) = 0.0288, max. residual density 0.552 $e{\cdot}Å^{-3}$, goodness-of-fit (F^2) = 1.023. CCDC No. 762538.

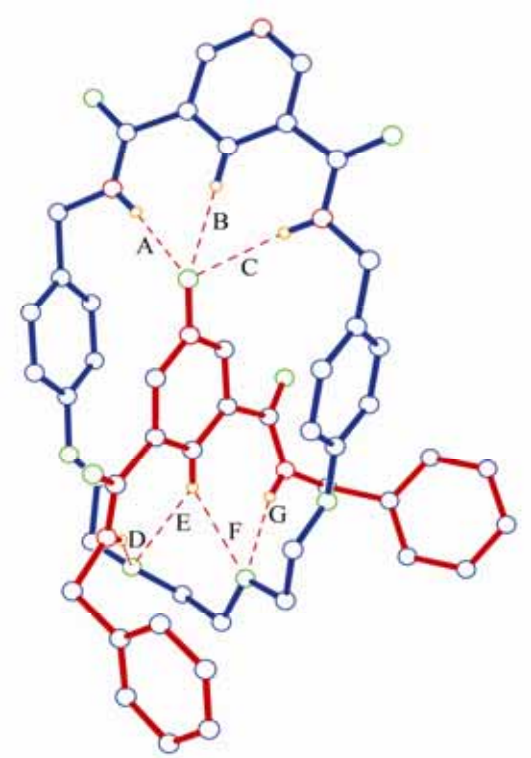


Figure S14. Ball-stick views of the X-ray structure of complex **2·3**. Macrocycle **2** is blue, pyridine N-oxide **3** is red, hydrogens are orange, oxygens are green, and nitrogen is red.

Hydrogens except that involved in hydrogen bonding have been omitted for clarity. Hydrogen-bond parameters: A): the distance of H···O is 2.266Å, the angle of N-H···O is 173.13 º, and the distance of N···O is 3.121Å. B): the distance of H···O is 2.149Å, the angle of C-H···O is 179.34 º, and the distance of C···O is 3.078Å. C): the distance of H···O is 2.288Å, the angle of N-H···O is 174.48 º, and the distance of N···O is 3.145Å. D): the distance of H···O is 2.203Å, the angle of N-H···O is 161.37 º, and the distance of N···O is 3.031Å. E): the distance of H···O is 2.613Å, the angle of C-H···O is 147.07 º, and the distance of C···O is 3.452Å. F): the distance of H···O is 2.335Å, the angle of C-H···O is 144.33 º, and the distance of C···O is 3.138Å. G): the distance of H···O is 2.218Å, the angle of N-H···O is 168.62 º, and the distance of N···O is 3.066Å.

X-ray analysis data of complex 2·3: Crystallographic data: block, colorless, 0.39×0.24×0.11 mm^3, $C_{48}H_{58}N_6O_{14}$, FW 943.00, Triclinic, space group P-1, a = 11.4699(13), b = 14.6930(16), c = 15.8590(17) Å, α = 113.824(2), β = 91.924(2), γ = 102.267(2)° , V = 2367.7(5) $Å^3$, Z = 2, D_c = 1.323 $g·cm^{-3}$, T = 298(2) K, μ = 0.098 mm^{-1}, 12379 measured reflections, 8521 independent reflections, 613 parameters, 0 restraints, F(000) = 1000, R_1 = 0.1349, wR_2 = 0.1691(all data), R_1 = 0.0603, wR_2 = 0.1310 [$I > 2\sigma(I)$], R(int) = 0.0331, max. residual density 0.294 $e·Å^{-3}$, goodness-of-fit (F^2) = 0.987. CCDC No. 762539.

6. Electrospray ionization mass spectra of the complexes

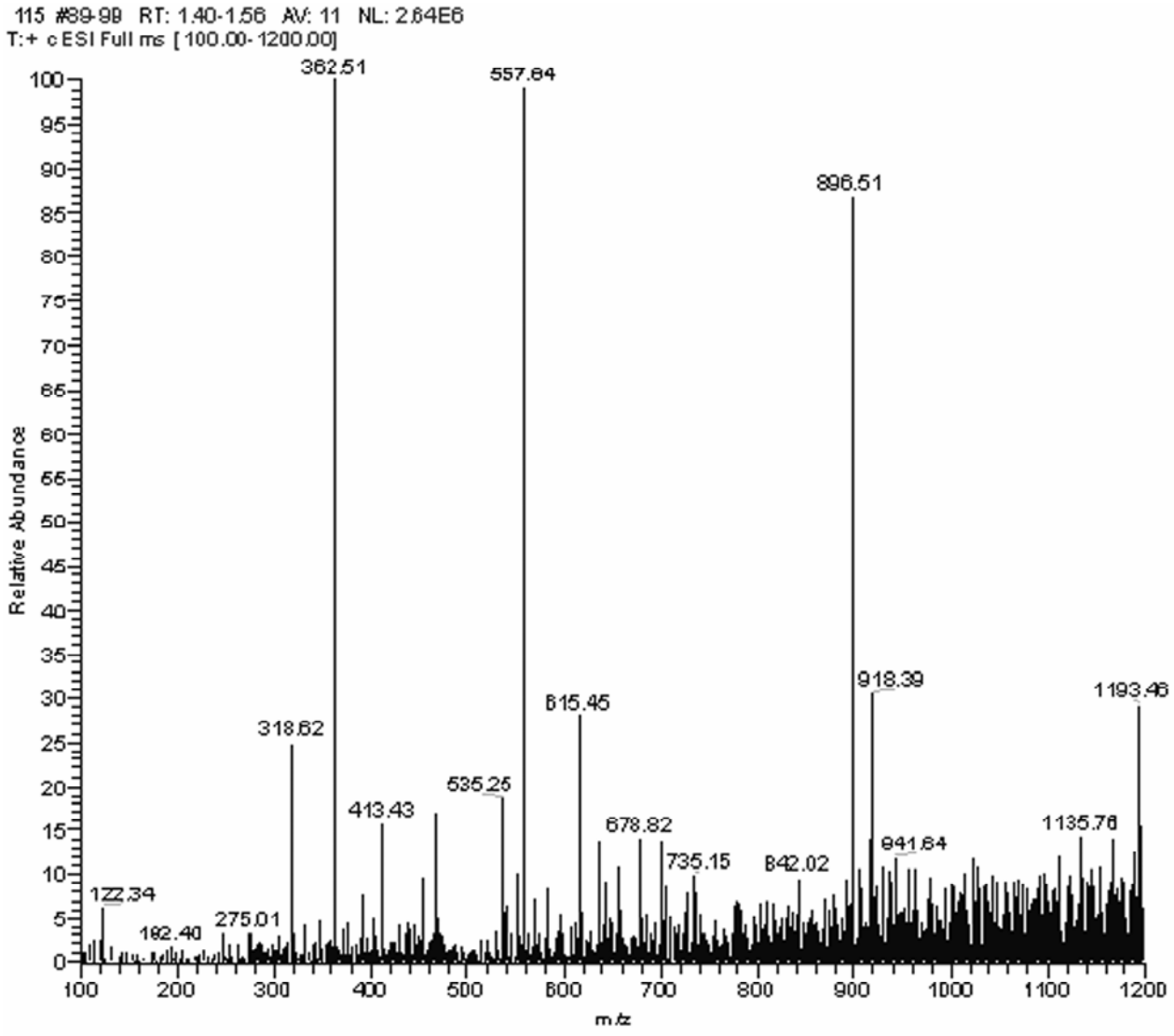


Figure S15. Low-resolution MS (ESI) spectrum of complex **1·3**. Assignment of main peaks: 362.51 [**3** + H]$^+$, 557.64 [**1** + Na]$^+$, 896.51 [**1·3** + H]$^+$.

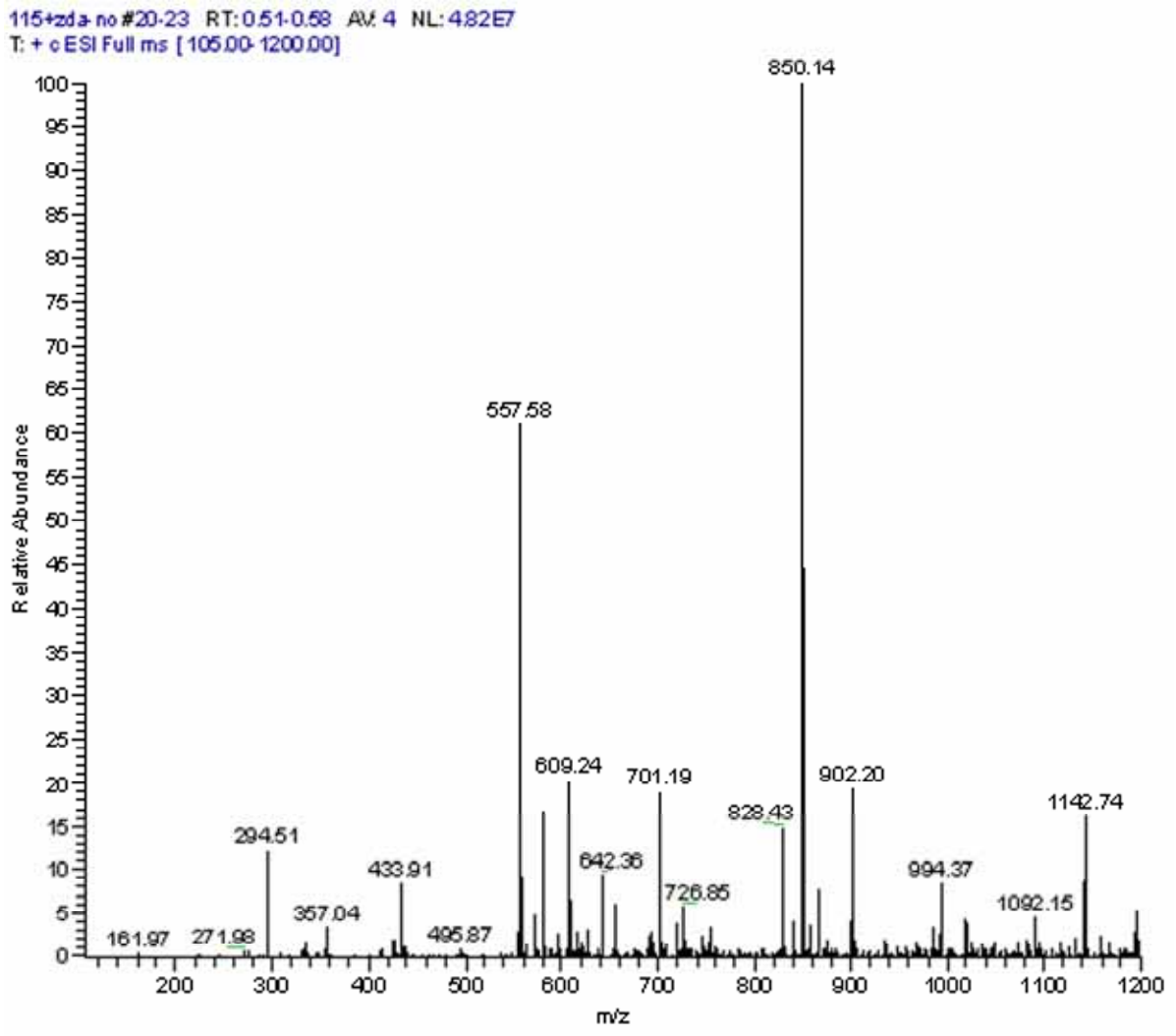


Figure S16. Low-resolution ESI-MS spectrum of complex **1·4**. Assignment of main peaks: 294.51 [**4** + H]$^+$, 557.58 [**1** + Na]$^+$, 609.24 [$\mathbf{4}_2$ + Na]$^+$, 850.14[**1·4** + Na]$^+$.

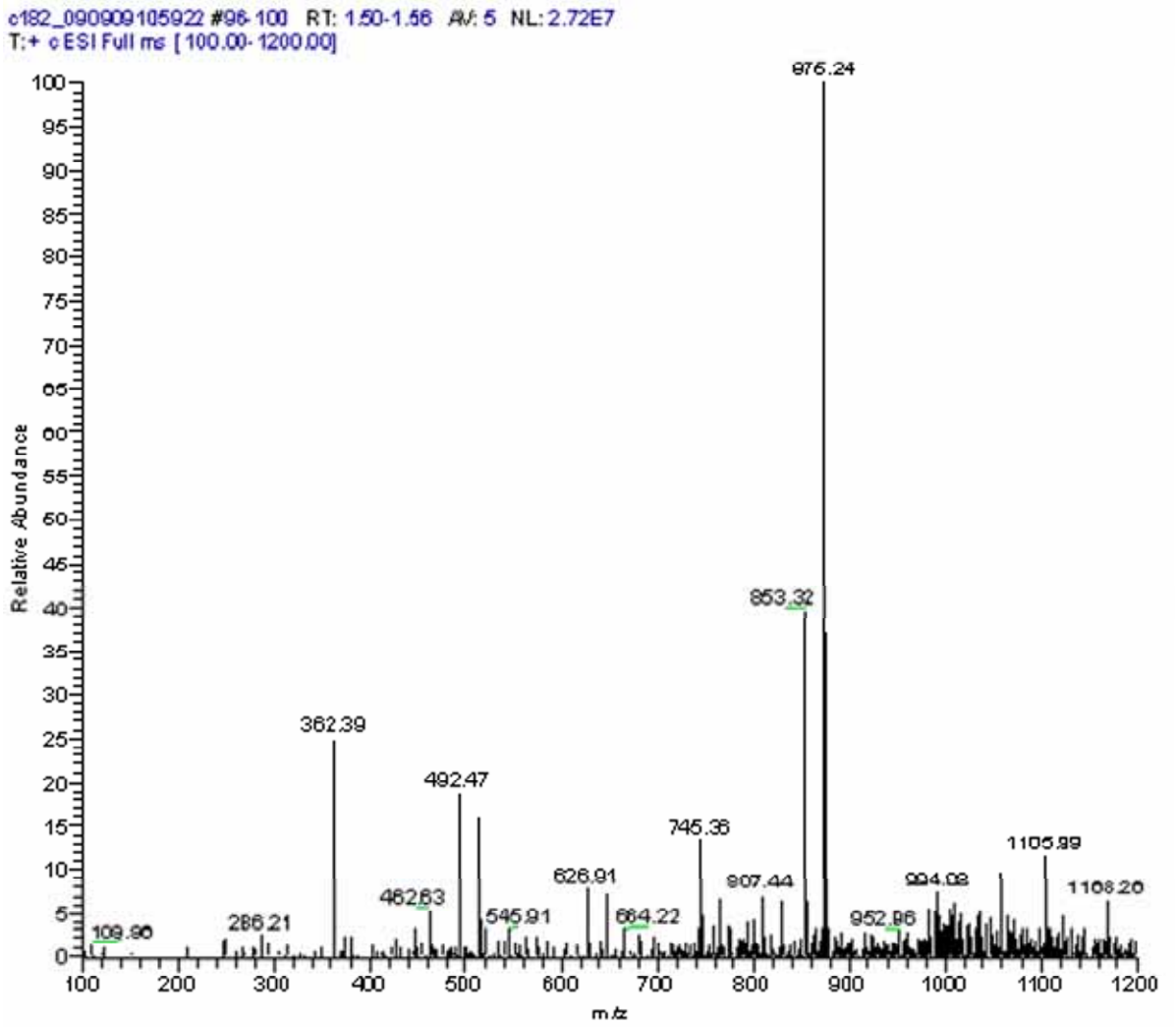


Figure S17. Low-resolution ESI-MS spectrum of complex **2·3**. Assignment of main peaks: 362.39 [**3** + H]$^+$, 492.47 [**2** + H]$^+$, 853.32 [**2·3** + H]$^+$, 875.34 [**2·3** + Na]$^+$.

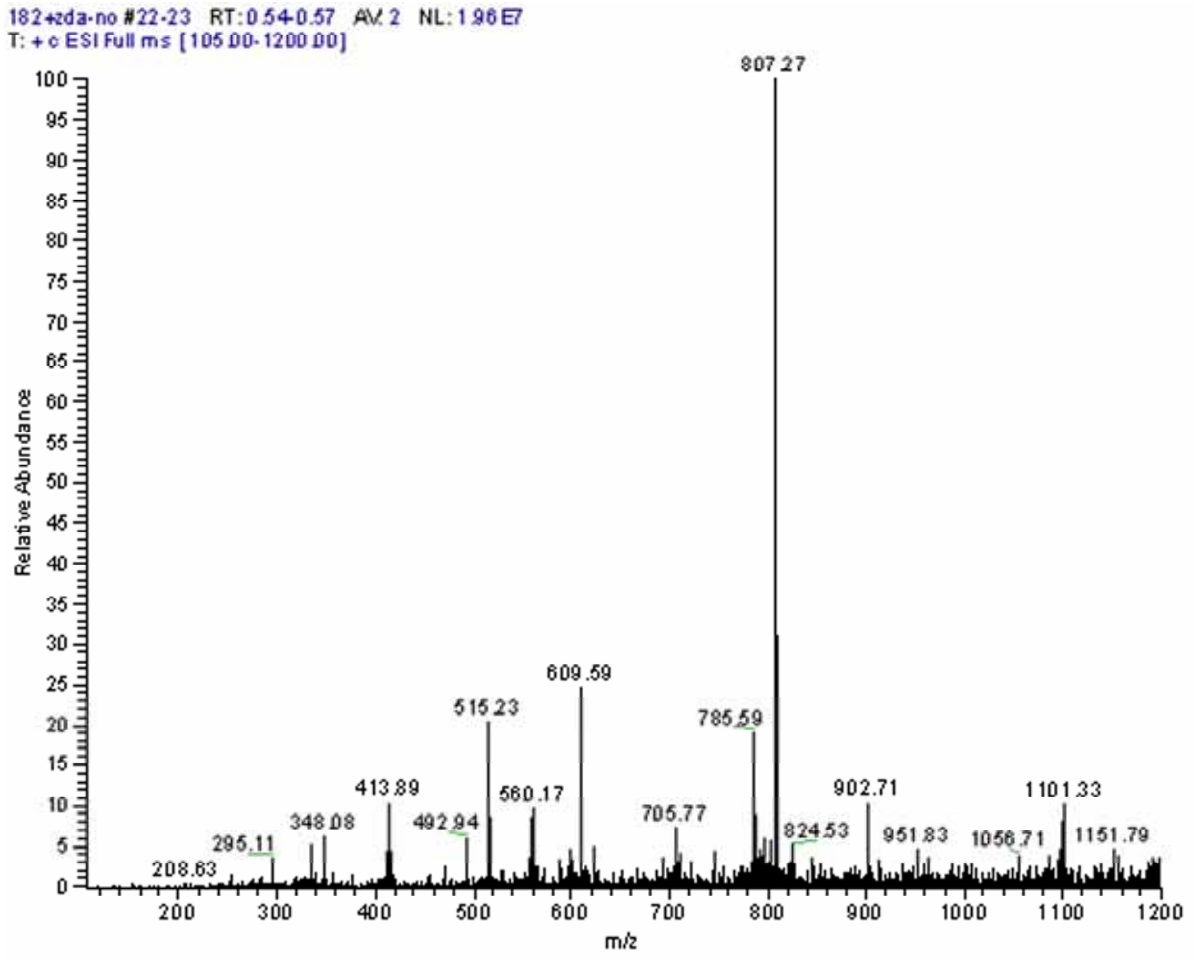


Figure S18. Low-resolution ESI-MS spectrum of complex **2·4**. Assignment of main peaks: 609.59 [$\mathbf{4}_2$ + Na]$^+$, 807.27[**2·4** + Na]$^+$.

7. References

[1] D.A.Leigh, A.R.Thomson, *Org. Lett.* **2006**, *8*, 5377–5379.

[2] C. Gong, P. B. Balanda, H.W. Gibson, *Macromolecules*, **1998**, *31*, 5278-5289.

[3] H.A.Benesi, J.H.Hildebrand, *J. Am. Chem. Soc.* **1949**, *71*, 2703-2707.

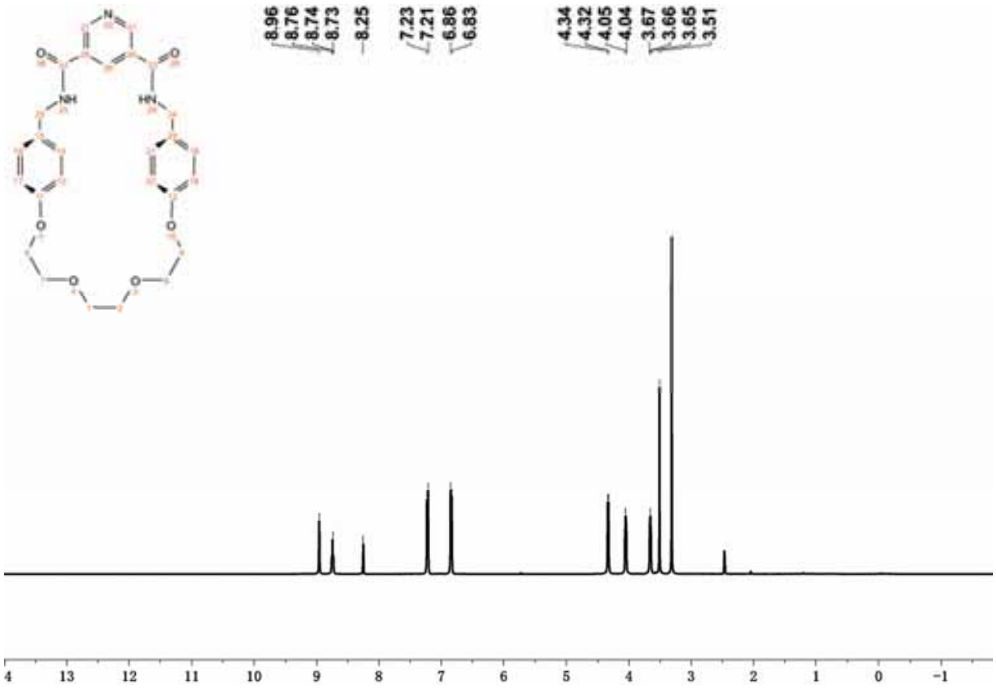


Figure S19. ^{1}H NMR spectrum of **2** in DMSO-*d*6 at 295K.

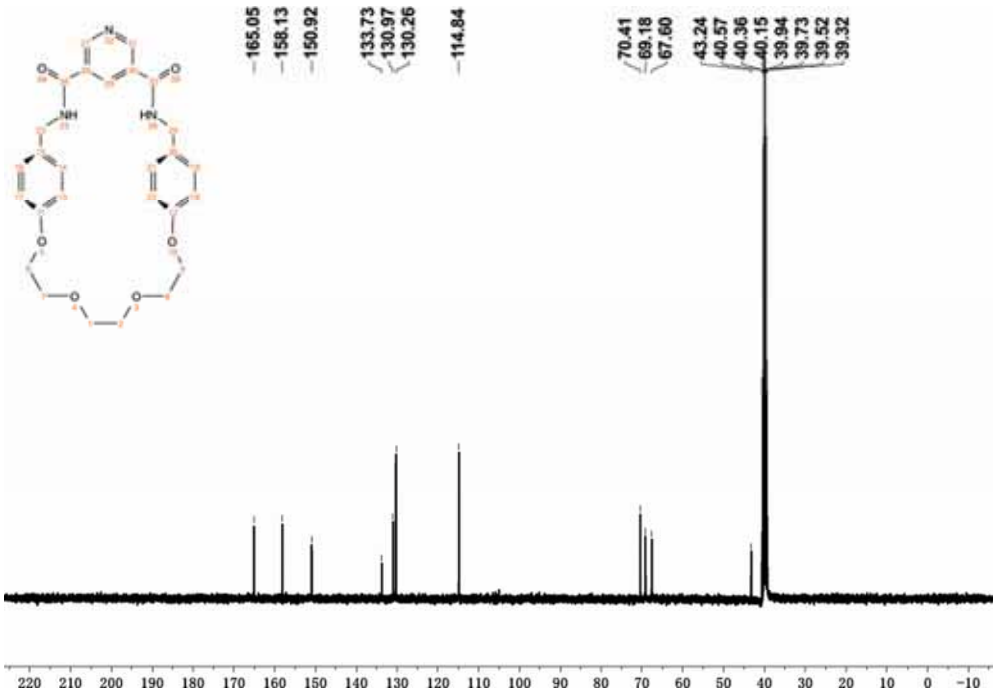


Figure S20. ^{13}C NMR spectrum of **2** in DMSO-*d*6 at 295K.

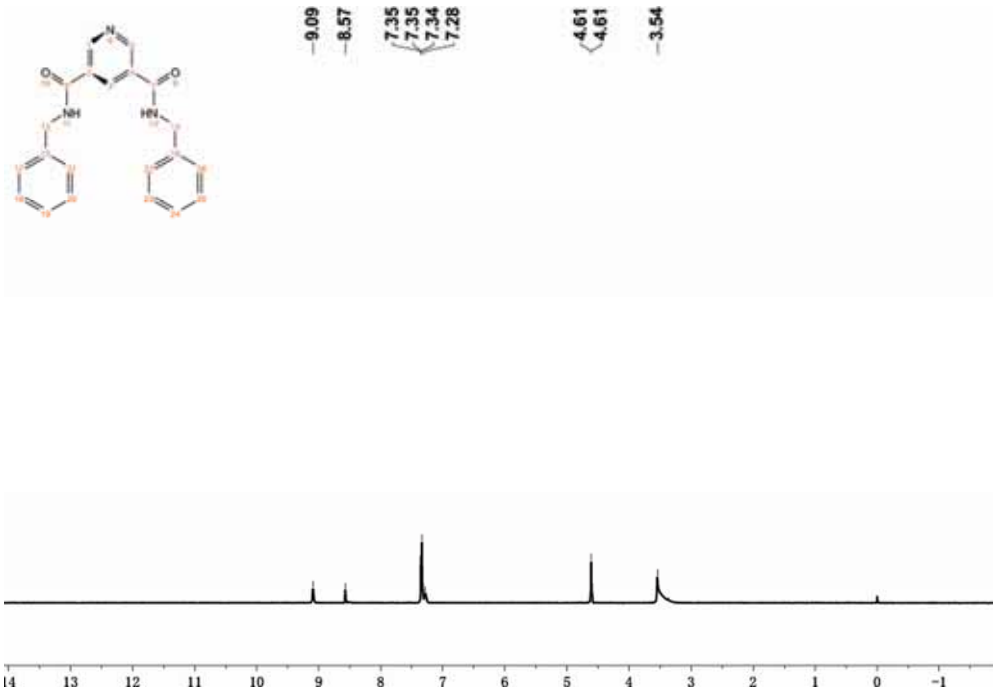


Figure S21. ^{1}H NMR spectrum of **3a** in $CD_3OD/CDCl_3$ (V: V=1:3).

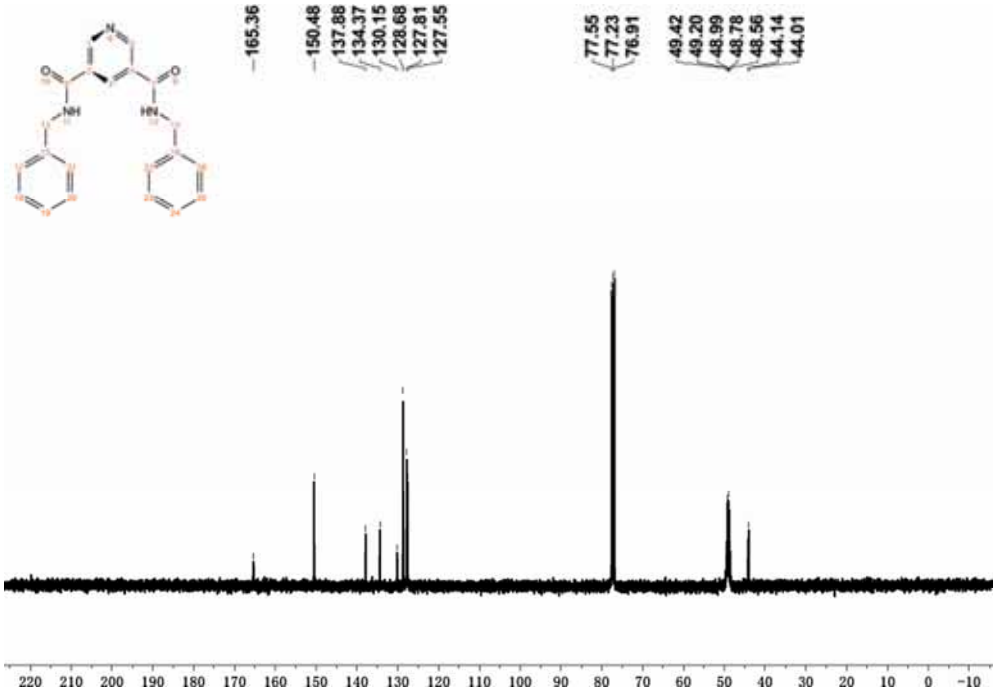


Figure S22. ^{13}C NMR spectrum of **3a** in $CD_3OD/CDCl_3$ (V: V=1:3).

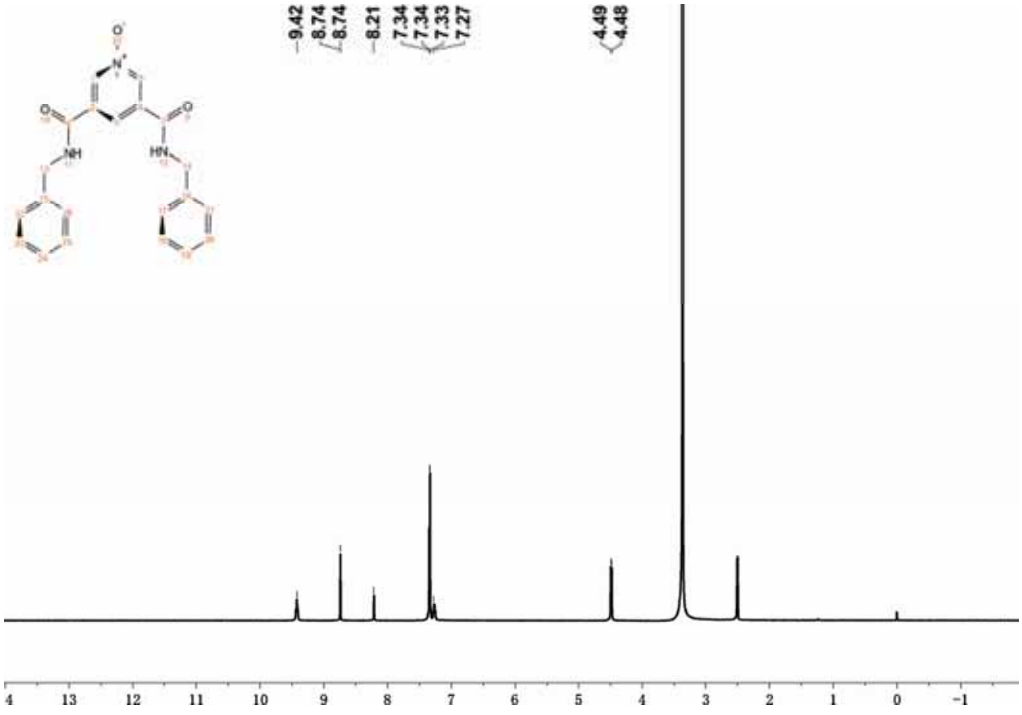


Figure S23. ^{1}H NMR spectrum of **3** in DMSO-*d*6 at 295K.

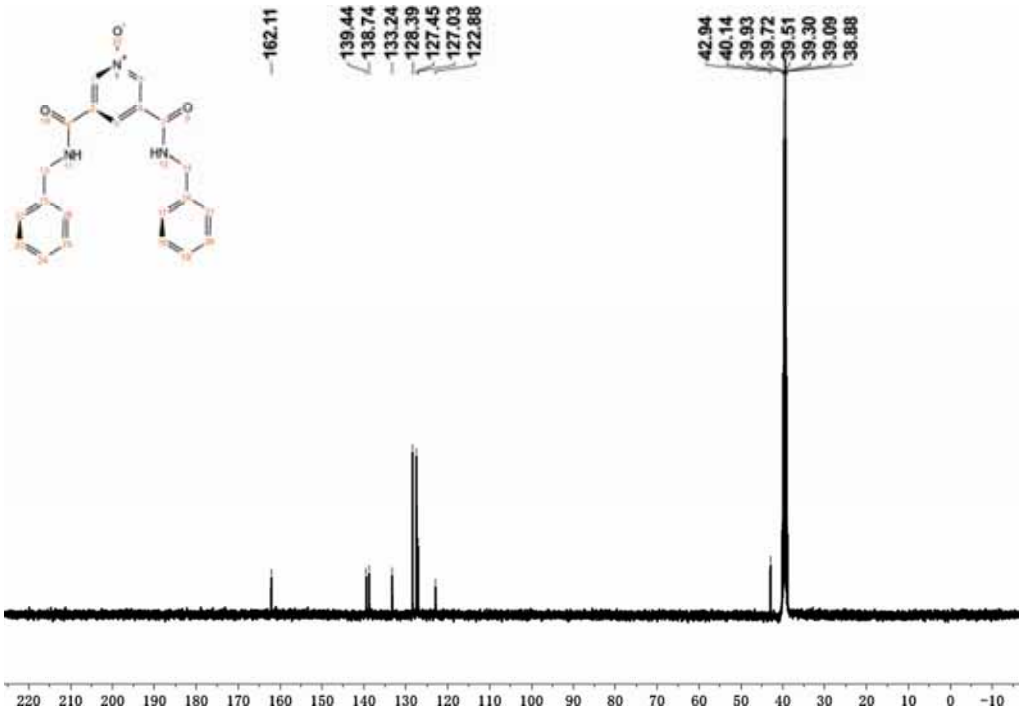


Figure S24. ^{13}C NMR spectrum of **3** in DMSO-*d*6 at 295K

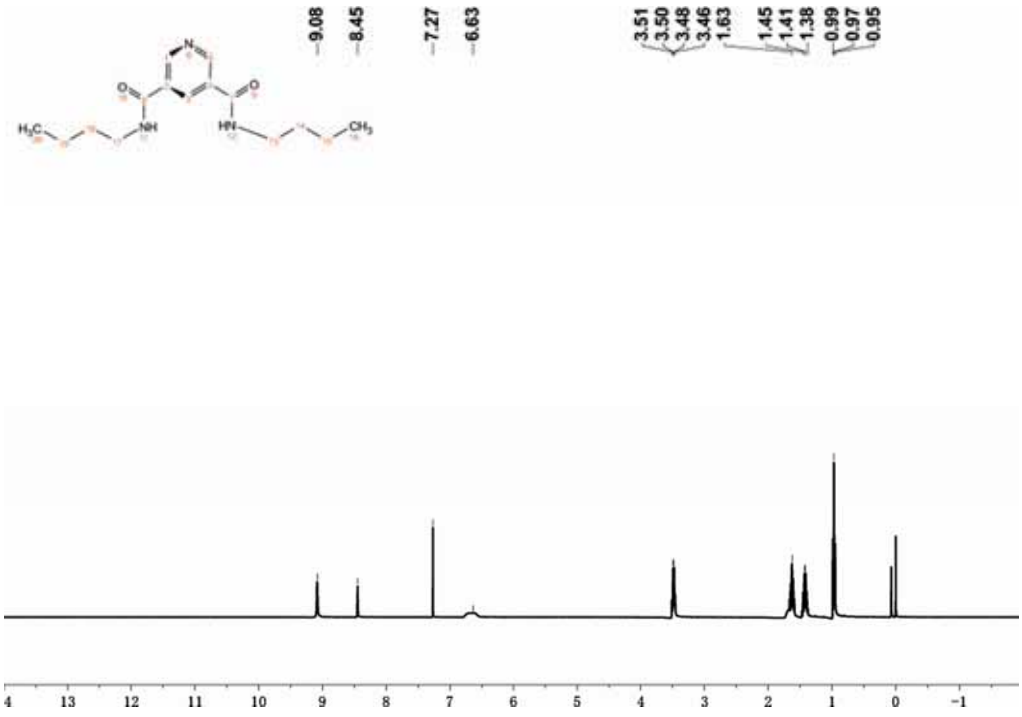


Figure S25. ^{1}H NMR spectrum of **4a** in $CDCl_3$ at 295K.

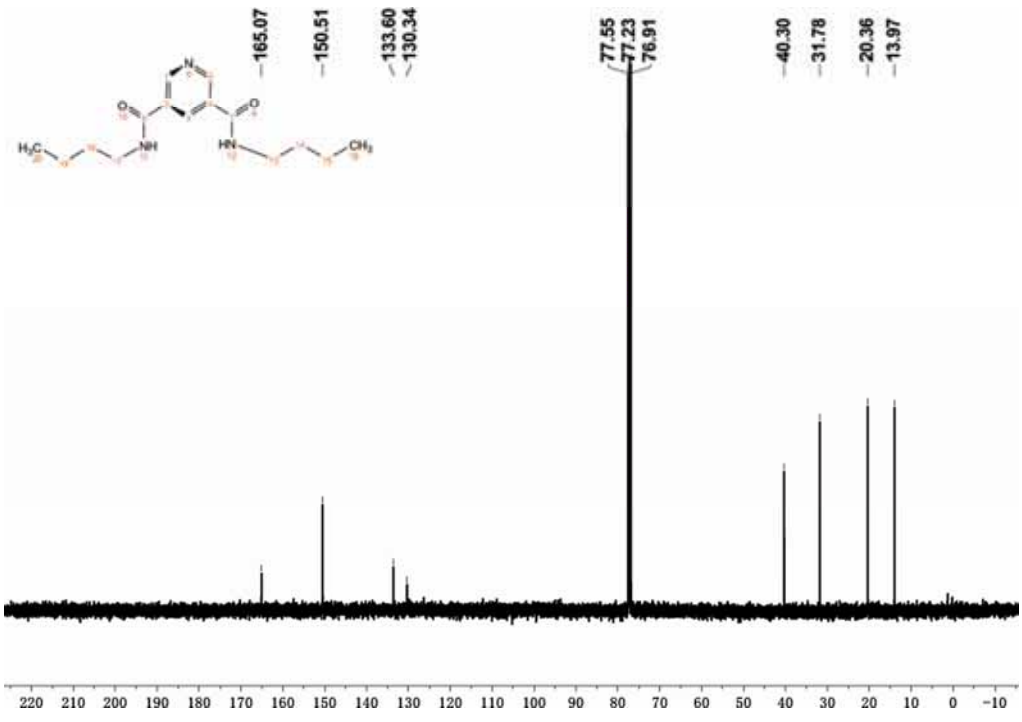


Figure S26. ^{13}C NMR spectrum of **4a** in $CDCl_3$ at 295K.

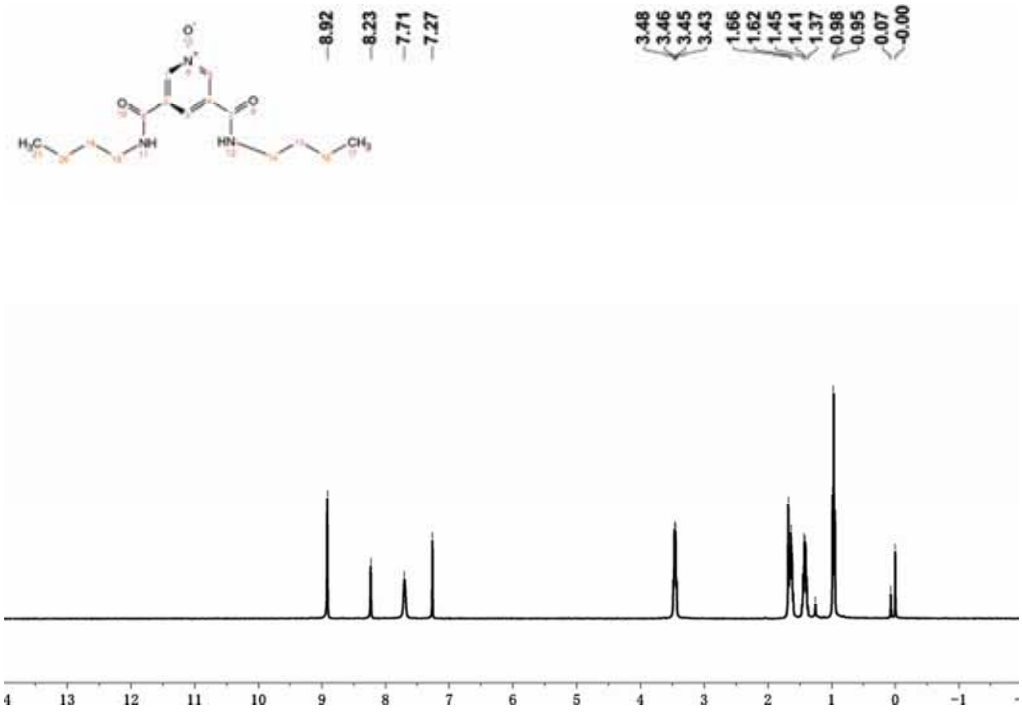


Figure S27. ^{1}H NMR spectrum of **4** in $CDCl_3$ at 295K.

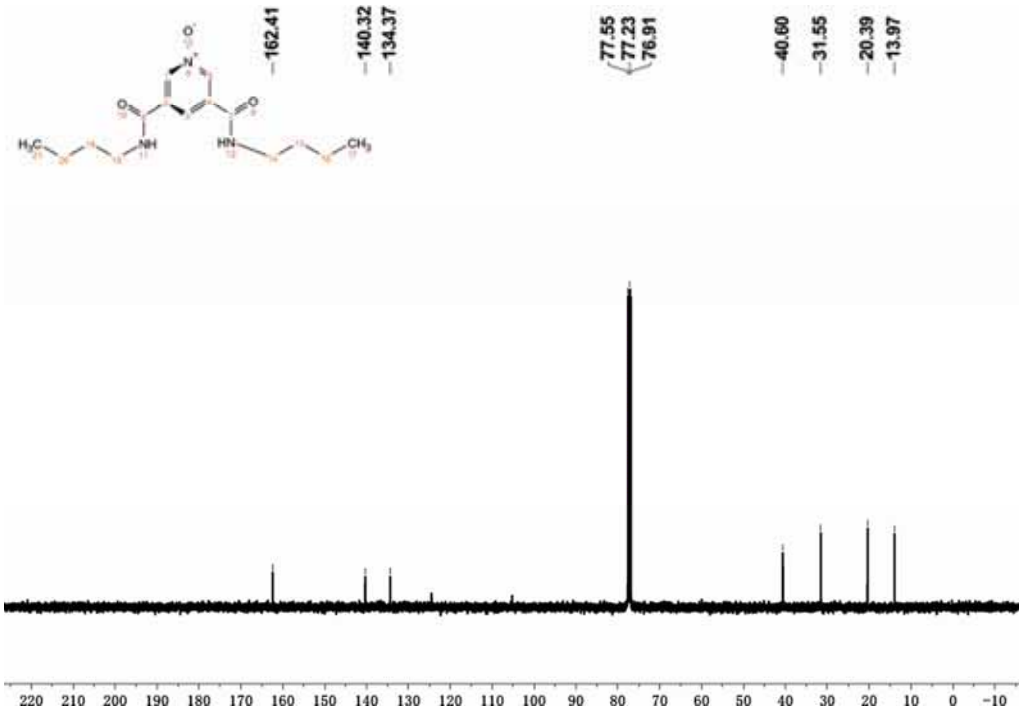


Figure S28. ^{13}C NMR spectrum of **4** in $CDCl_3$ at 295K.

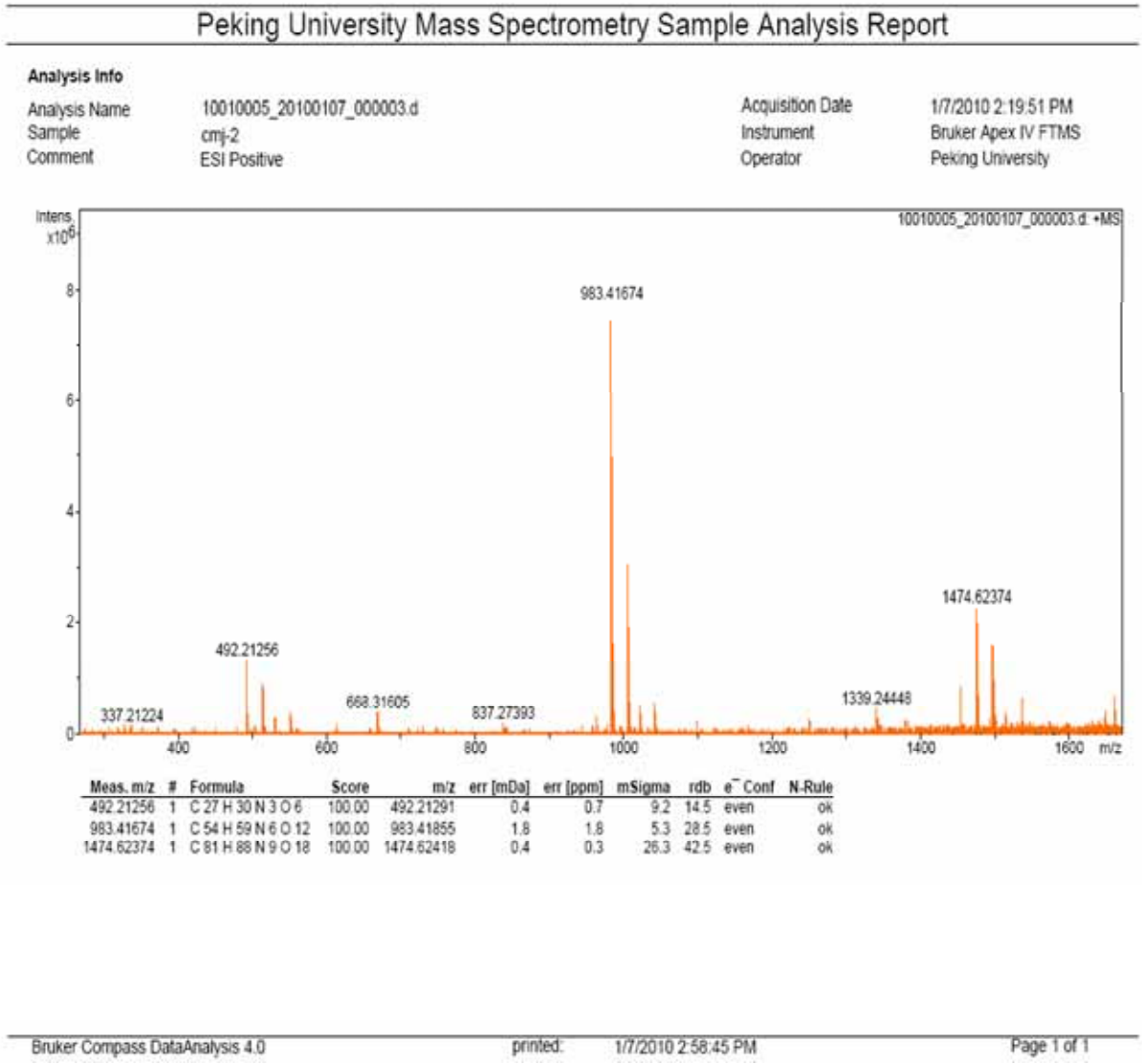


Figure S29. HR-MS(ESI) spectrum of macrocycle **2**, 492.2126 [**2** + H] $^{+}$, 983.4167[$\mathbf{2}_2$ + H]$^{+}$, 1474.6237 [$\mathbf{2}_3$ + H]$^{+}$.

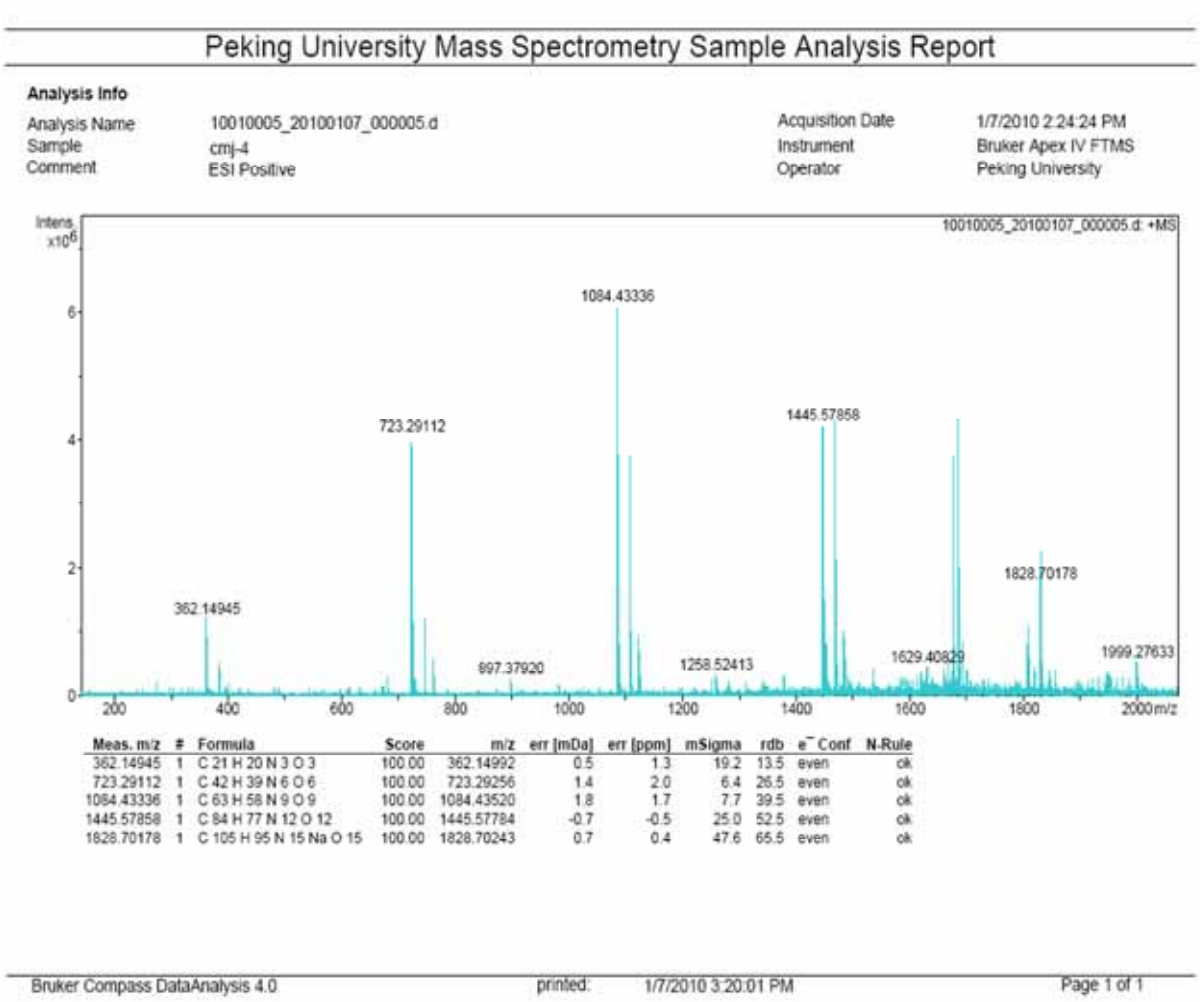


Figure S30. HR-MS (ESI) spectrum of **3**, 362.1495 [**3** + H]$^+$, 723.2911 [$\mathbf{3}_2$ + H]$^+$, 1084.4334 [$\mathbf{3}_3$ + H]$^+$, 1445.5786 [$\mathbf{3}_4$ + H]$^+$, 1828.7018 [$\mathbf{3}_5$ + H]$^+$.

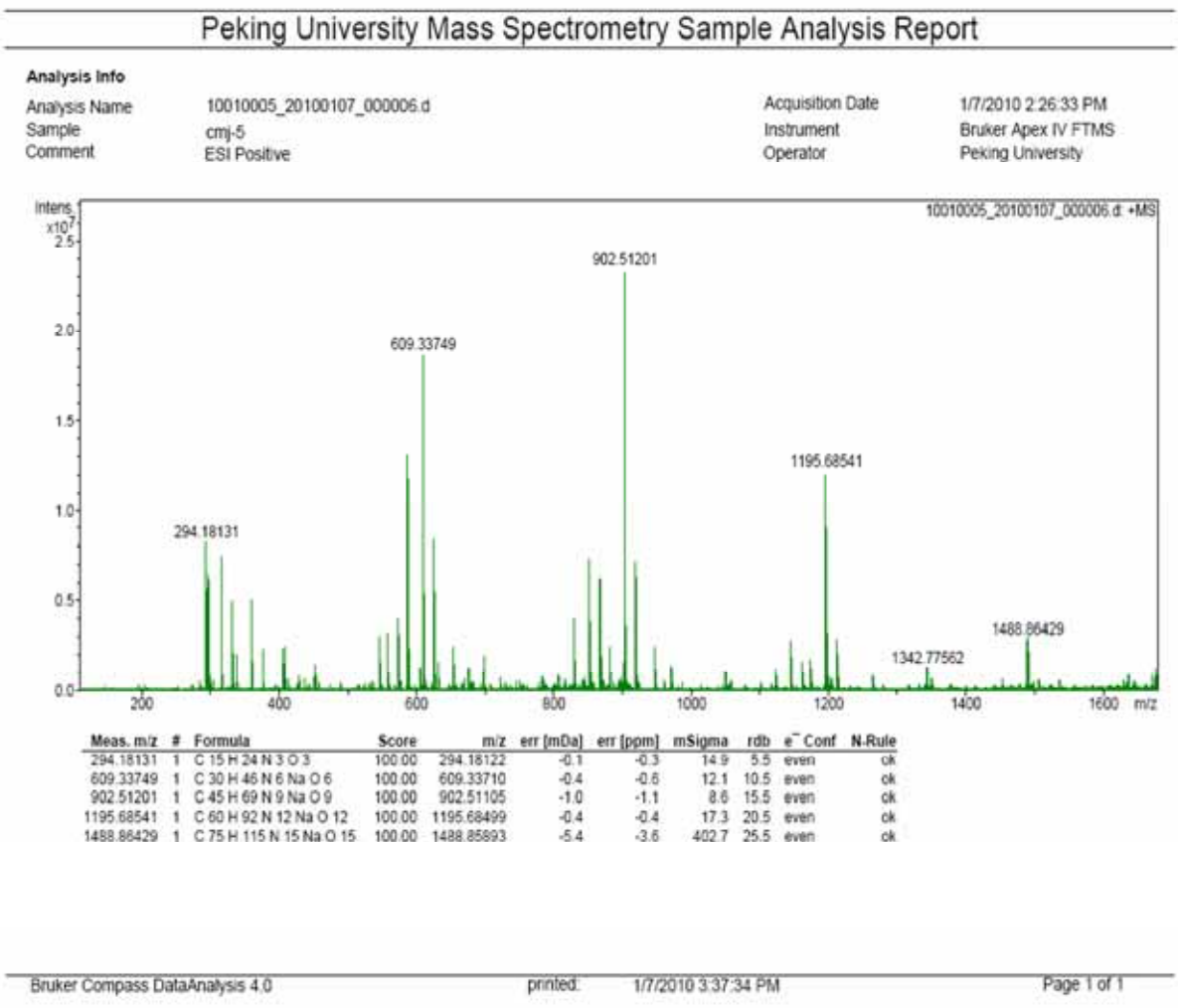


Figure S31. HR-MS (ESI) spectrum of **4**,294.1813 [**4** + H] $^{+}$, 609.3375 [$\mathbf{4}_2$ + Na] $^{+}$, 902.5120 [$\mathbf{4}_3$ + Na]$^{+}$,1195.6854 [$\mathbf{4}_4$ + Na]$^{+}$, 1488.8643 [$\mathbf{4}_5$ + Na]$^{+}$.