Electronic Supplementary Information

Electron-Deficient Supramolecular Macrocyclic Host for the Selective Separation of Aromatics and Cyclic Aliphatics

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Contents

1. **Materials and Methods.....S2**
2. **Synthesis of New compounds. S2**
3. **^{1}H NMR and ^{13}C NMR Spectral of New compounds. S4**
4. **Thermogravimetric analysis of host 1.....S6**
5. **Stability test S6**
6. **Photos of prepared column S7**
7. **Crystal data for 1 .....S7**
8. **Crystal data $(PhH)_2$@1.....S8**
9. **Crystal data for Tol_2@1. .....S9**
10. **Determination of the Association Constants of the Complexes. S9**

1. Materials and Methods.

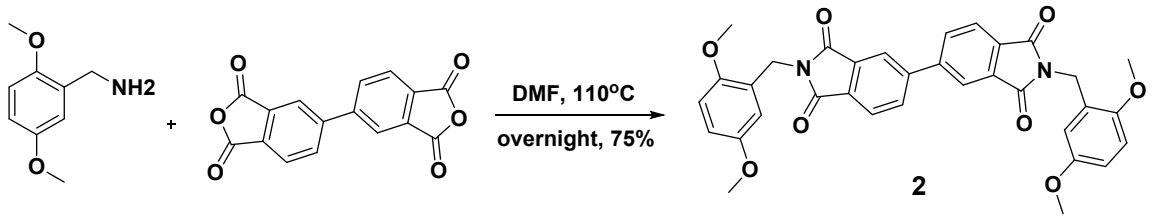
All reactions were carried out with oven-dried glassware. Commercial reagents were used without further purification. Flash column chromatography was performed on 100-200 mesh silica gel. ^{1}H NMR, ^{13}C NMR spectra were recorded on a Bruker DMX400 NMR spectrometer. Melting points were determined using WRR melting point apparatus and were uncorrected. High-resolution mass spectra (HRMS) were determined on Bruker Daltonics Inc. APEXIII 7.0 TESLA FTMS. The single crystal X-ray data were measured by direct methods using Bruker SMART APEX II.

Thermogravimetric analysis (TGA) was carried out using a Q5000IR analyzer (TA Instruments) with an automated vertical overhead thermobalance. The samples were heated at 10 °C/min using N2 as the protective gas.

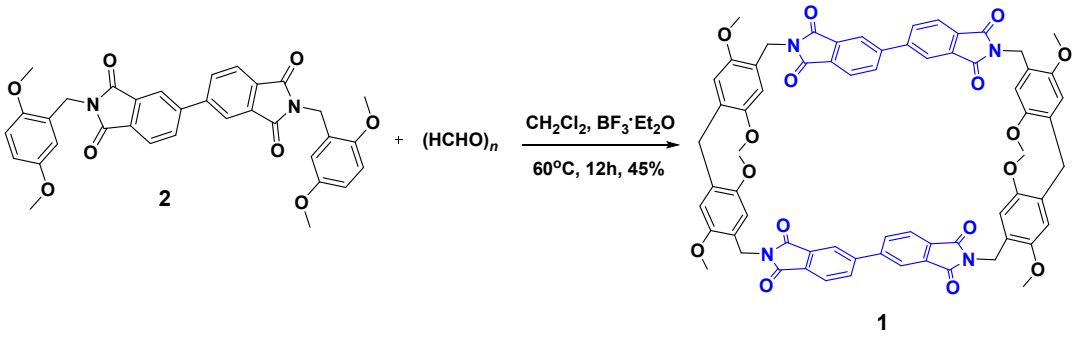
Column packing procedure for GC separation.

The host **1** packed column was prepared by manual filling. The **host 1** (100 mg) was fist dissolved in 15 mL chloroform, then 2g 40-60 mesh red carrier 6201 was added. The above mixture was dried under vacuo and the residue was dried at 120 °C for another 4 h. Carrier that laoded with host **1** was packed into a 1.0 m long, 2.0 mm i.d. stainless steel column. During the filling process, the column was continuously tapped and the packing was compacted, and then the host **1** packed column was obtained. After the column was loaded into the column box, it was activated under 120 °C for 12 hours before use. GC experiments were performed on the Fuli 9790II GC system, the flow rate of carrier gas was 25 ml/min, the injection volume of sample was 0.1 uL.

2. Synthesis of New compounds.



Compound 2 3,3',4,4'-biphenyltetracarboxylic dianhydride (1.47 g, 5 mmol) and 2,5-dimethoxybenzylamine (2.01 g, 12 mmol) were dissolved with anhydrous DMF (35 mL) in a sealed tube and then heated at 110 °C for 12 h on an oil bath. After being cooled to room temperature, the reaction mixture was poured into the water and the resulting yellow-green precipitate was washed with water and then dried under vacuum to afford compound **2** (2.22 g, yield 75%) as yellow solid. M.p.: >300 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (s, 2H), 7.99 (d, *J* = 7.9 Hz, 4H), 6.81 (d, *J* = 9.9 Hz, 2H), 6.76 (d, *J* = 6.7 Hz, 4H), 4.92 (s, 4H), 3.83 (s, 6H), 3.73 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.53, 153.47, 151.37, 145.18, 133.37, 132.94, 131.94, 125.18, 124.18, 122.20, 115.15, 112.56, 111.49, 56.11, 55.73, 37.07. HRMS (APCI) m/z: $[M+H]^+$ calcd for $C_{34}H_{29}N_2O_8$, 593.1924; found, 593.1928.



Host 1 To a mixture of **2** (1.18 g, 2.0 mmol) and paraformaldehyde (180 mg, 6.0 mmol) in dichloromethane (150 mL) was added boron trifluoride diethyl etherate (0.3 mL, 2.4 mmol). The mixture was stirred at 60 °C for 12 h. Then the reaction was quenched by the addition of 150 mL water. The organic layer was separated and dried with anhydrous $MgSO_4$. The solvent was removed in vacuo and the residue was separated by column chromatography on silica gel (eluent: 1:15 ethyl acetate /DCM) to give **1** (544 mg, 45%) as yellow-green solids. M.p.: >300 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (s, 4H), 7.86 (t, *J* = 5.9 Hz, 8H), 6.90 (s, 4H), 6.69 (s, 4H), 4.85 (s, 8H), 3.87 (s, 4H), 3.76 (s, 12H), 3.69 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.56, 167.19, 151.26, 144.92, 133.32, 132.68, 131.86, 129.86, 123.88, 122.17, 121.80, 114.26, 113.50, 56.30, 56.11, 37.36,

30.23. HRMS (APCI) m/z: $[M+H]^+$ calcd for $C_{70}H_{57}N_4O_{16}$, 1209.3770; found, 1209.3784.

3. ^{1}H NMR and ^{13}C NMR Spectral of New compounds.

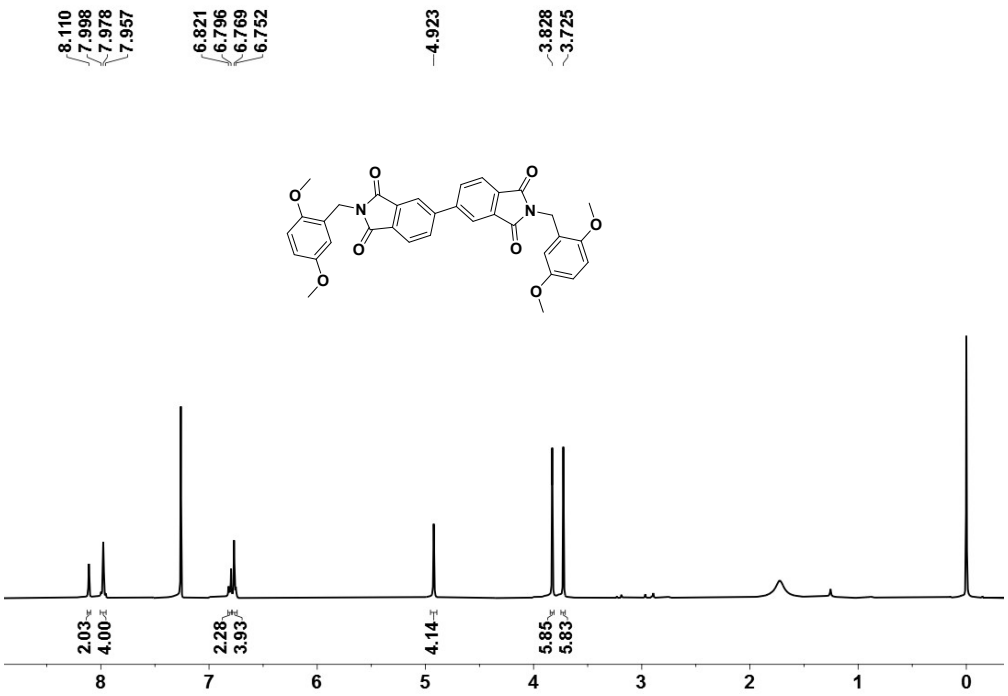


Figure S1. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of **2**.

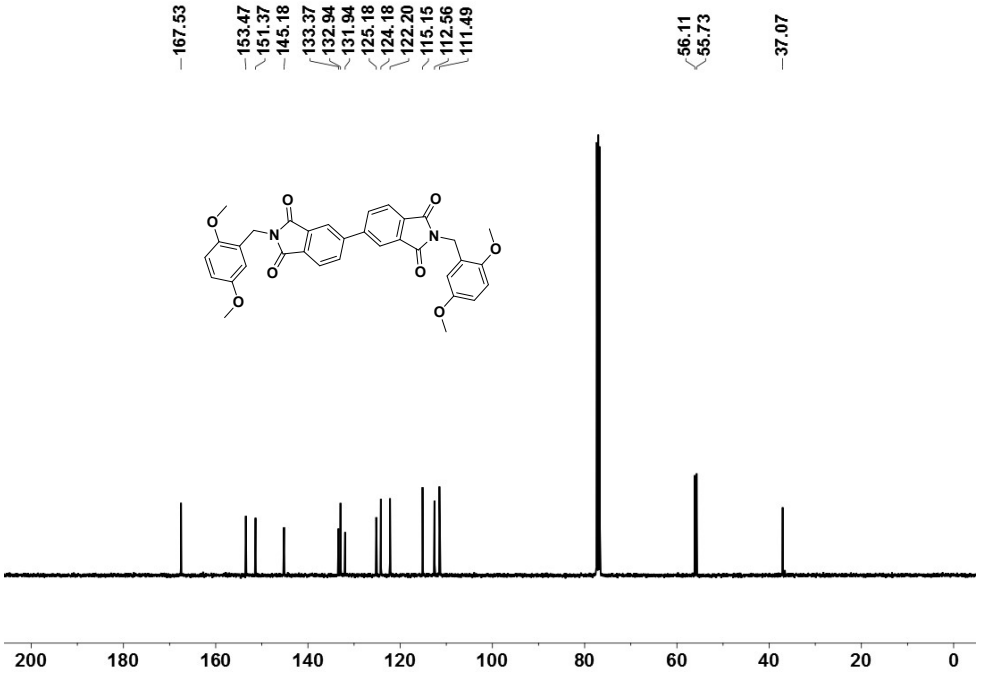


Figure S2. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298K) of **2**.

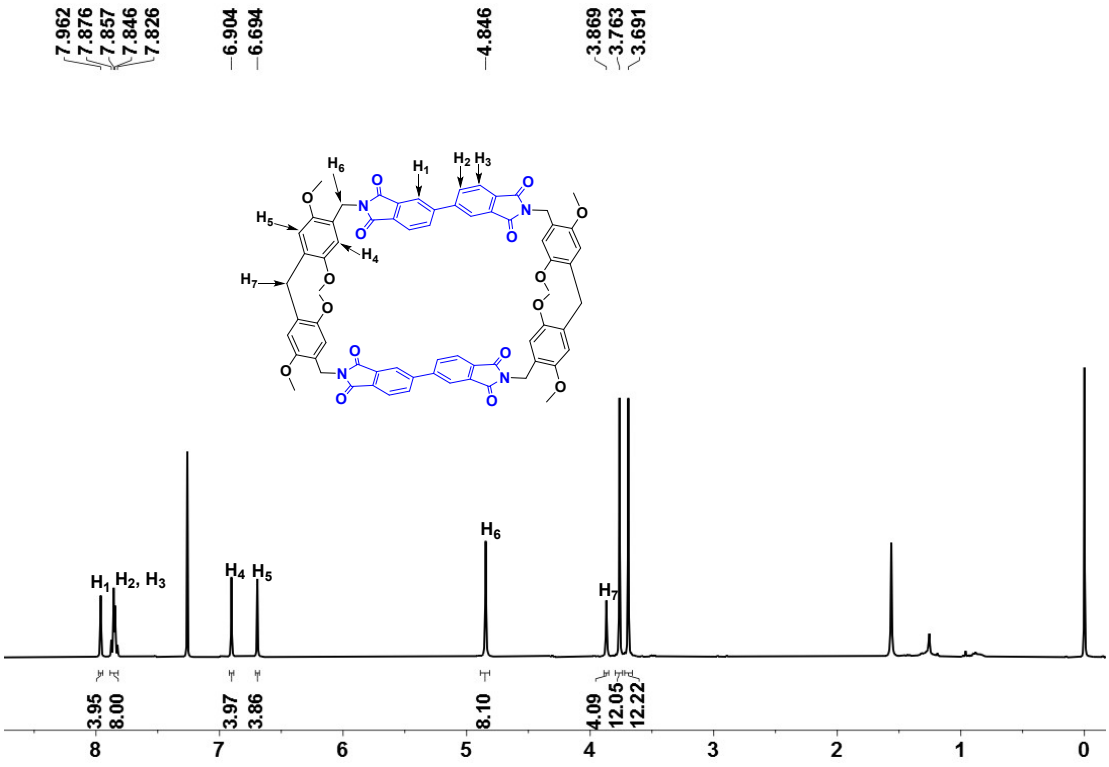


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298K) of host **1**.

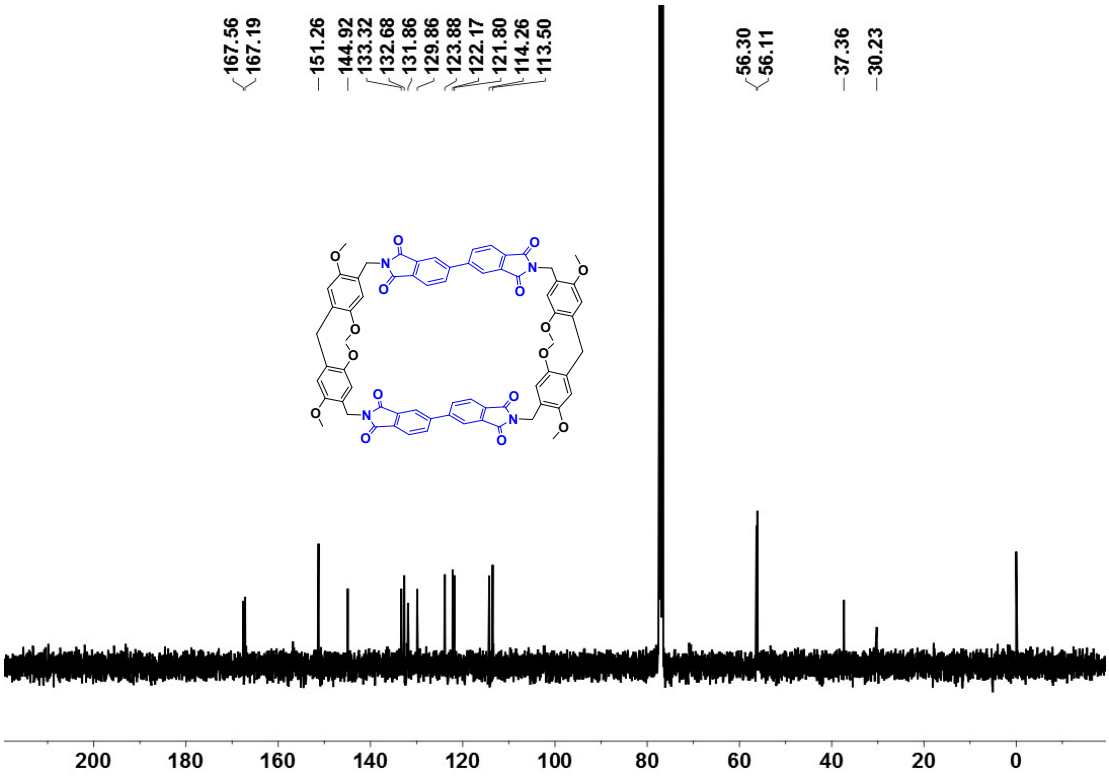


Figure S4. ^{13}C NMR spectrum (101 MHz, $CDCl_3$, 298K) of host **1**.

4. Thermogravimetric analysis of host 1

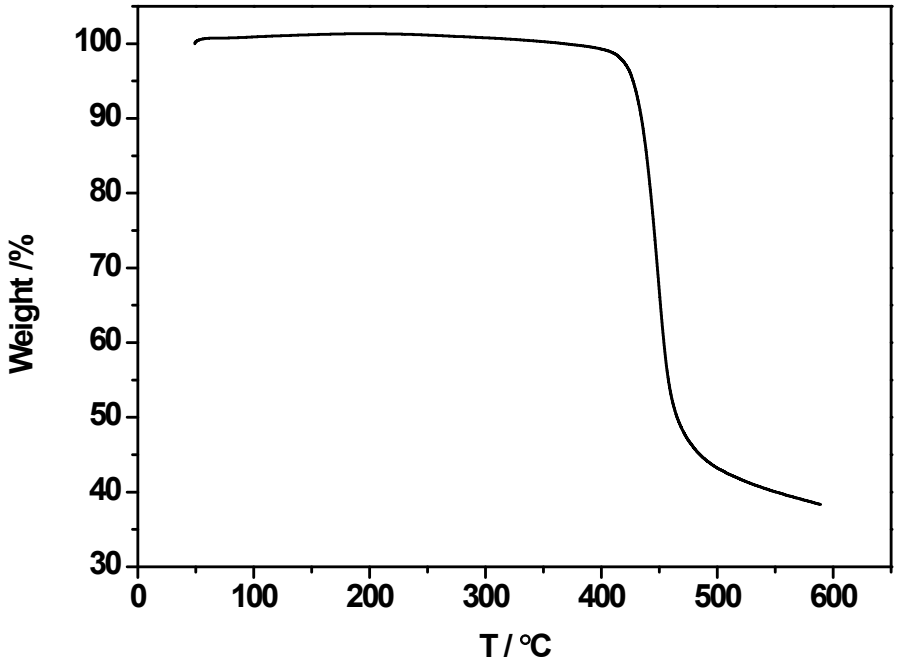


Figure S5. Thermogravimetric analysis of **1**.

5. Stability test

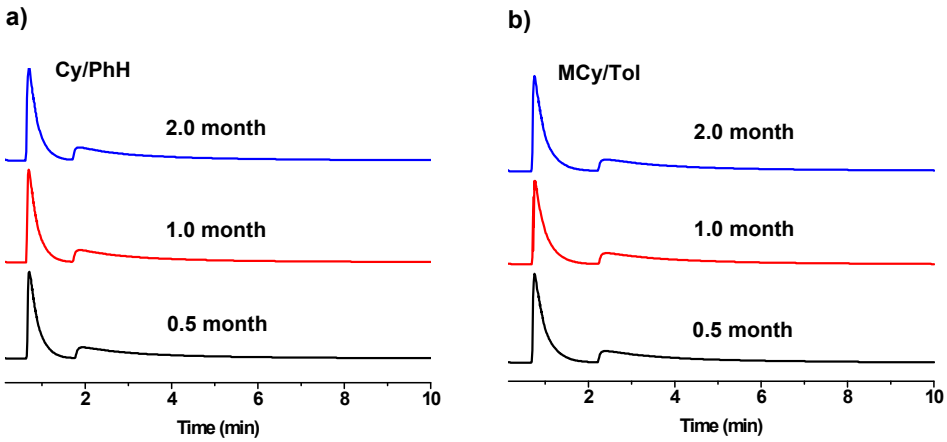


Figure S6. GC chromatograms of (a) cyclohexane/benzene (1/1, V/V) and (b) methylcyclohexane/toluene (1/1, V/V) on the **host 1** packed column obtained after two months on the same column using the same conditions, respectively.

6. Photos of prepared column

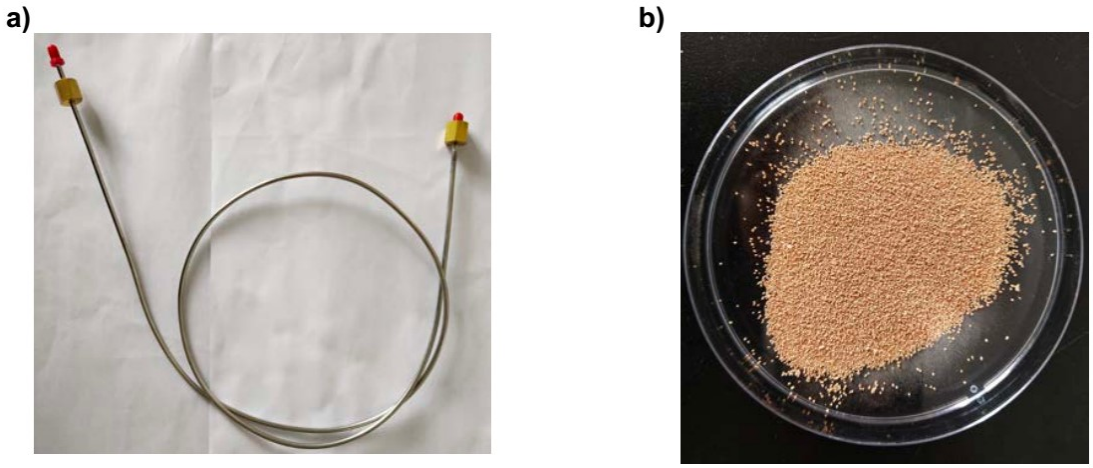


Figure S7. (a) photo of host **1** packed column. (b) red carrier 6201 that loaded 5% wt host **1**.

7. Crystal data for 1

Identification code	11_a
Empirical formula	$C_{36}H_{29}Cl_3N_2O_8$
Formula weight	723.96
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	9.344(6)
b/Å	12.709(8)
c/Å	15.488(9)
α/°	77.638(6)
β/°	80.102(6)
γ/°	87.490(6)
Volume/Å^3	1769.8(19)
Z	2
ρ_{calc}g/cm^3	1.358
μ/mm^{-1}	0.312
F(000)	748.0
Crystal size/mm^3	0.42 × 0.23 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.73 to 55.214

Index ranges	$-12 \leq h \leq 12$, $-16 \leq k \leq 16$, $-20 \leq l \leq 19$
Reflections collected	16687
Independent reflections	7737 [$R_{int} = 0.0430$, $R_{sigma} = 0.0744$]
Data/restraints/parameters	7737/0/446
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	$R_1 = 0.0871$, $wR_2 = 0.2421$
Final R indexes [all data]	$R_1 = 0.1661$, $wR_2 = 0.3003$
Largest diff. peak/hole / e Å^{-3}	0.73/-0.66

8. Crystal data $(PhH)_2$@1

Identification code	11
Empirical formula	$C_{82}H_{70}N_4O_{16}$
Formula weight	1367.42
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	9.468(7)
b/Å	13.913(10)
c/Å	16.060(12)
α/°	96.956(10)
β/°	95.231(10)
γ/°	94.568(9)
Volume/Å^3	2083(3)
Z	1
ρ_{calc}g/cm^3	1.090
μ/mm^{-1}	0.076
F(000)	718.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.962 to 52.99
Index ranges	-11 ≤ h ≤ 11, -17 ≤ k ≤ 17, -20 ≤ l ≤ 20
Reflections collected	22184
Independent reflections	8537 [R_{int} = 0.0392, R_{sigma} = 0.0565]
Data/restraints/parameters	8537/252/494
Goodness-of-fit on F^2	0.968
Final R indexes [I>=2σ (I)]	R_1 = 0.0731, wR_2 = 0.2016
Final R indexes [all data]	R_1 = 0.1204, wR_2 = 0.2413
Largest diff. peak/hole / e Å^{-3}	0.55/-0.25

9. Crystal data for Tol_2@1.

Identification code	22050921
Empirical formula	$C_{84}H_{72}N_4O_{16}$
Formula weight	1393.45
Temperature/K	293(2)
Crystal system	triclinic

Space group	P-1
a/Å	9.332(3)
b/Å	12.278(3)
c/Å	15.500(3)
α/°	77.024(17)
β/°	82.21(2)
γ/°	86.73(2)
Volume/Å^3	1713.9(7)
Z	1
ρ_{calc}g/cm^3	1.350
μ/mm^{-1}	0.094
F(000)	732.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.406 to 49.996
Index ranges	-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -18 ≤ l ≤ 18
Reflections collected	15483
Independent reflections	5994 [R_{int} = 0.1135, R_{sigma} = 0.1576]
Data/restraints/parameters	5994/202/490
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.1199, wR_2 = 0.2695
Final R indexes [all data]	R_1 = 0.2770, wR_2 = 0.3469
Largest diff. peak/hole / e Å^{-3}	0.43/-0.36

10. Determination of the Association Constants of the Complexes.

In the ^{1}H NMR titrations, $CDCl_3$ was chosen to dissolve the host and the guests. Chemical shifts were reported in parts per million (*ppm*). By a mole ratio plot, each stoichiometry was determined. Titration curve-fitting and association constant values were calculated by employing the BindFit program developed by Prof. Pall Thordarson of UNSW. 1:2 Binding stoichiometry was chosen in the BindFit program. This program employs a nonlinear least-squares regression analysis and is available free of cost online through the following link: http://supramolecular.org.

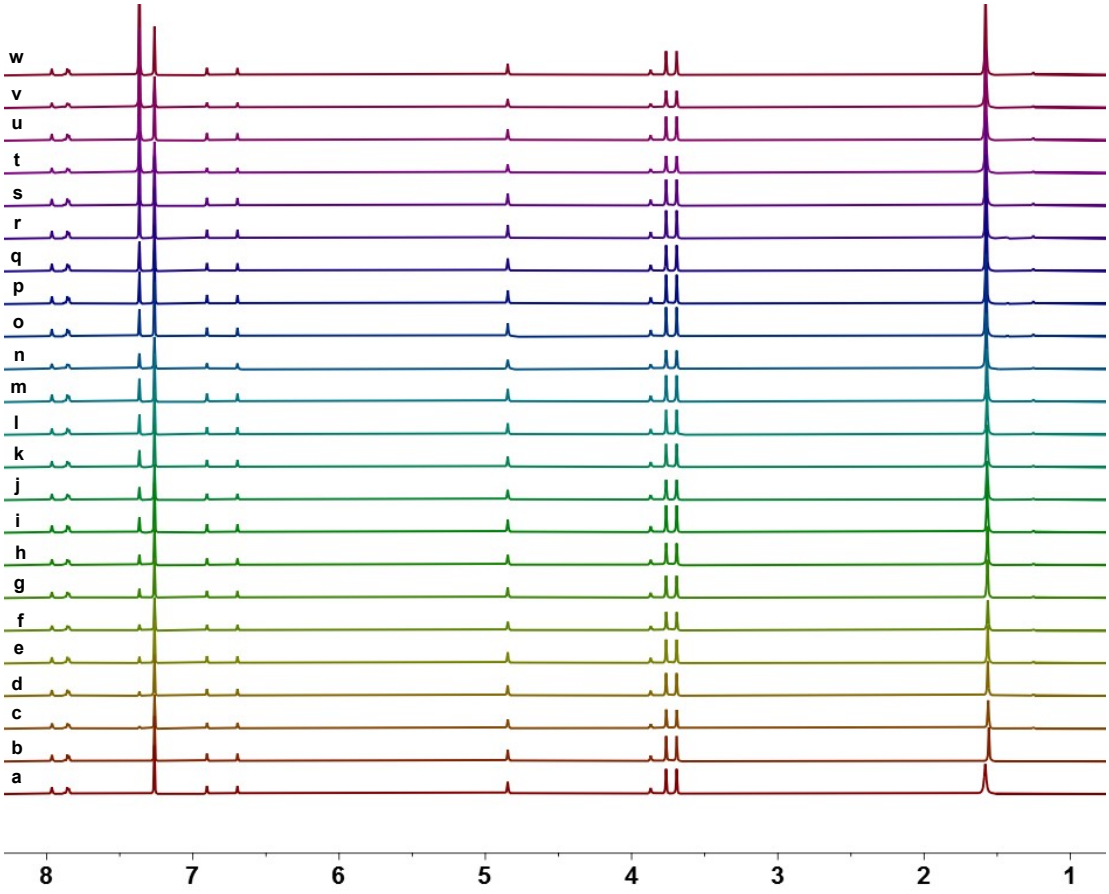


Figure S8. ^{1}H NMR spectra (400 MHz, $CDCl_3$, v/v, 298 K) of **1** at a concentration of 1.0 mM with different concentrations of **PhH**: (a) 0.00 mM; (b) 0.2 mM; (c) 0.4 mM; (d) 0.6 mM; (e) 0.8 mM; (f) 1.0 mM; (g) 1.2 mM; (h) 1.4 mM; (i) 1.6mM; (j) 1.8 mM; (k) 2.0 mM; (l) 2.2 mM; (m) 2.4 mM; (n) 2.6 mM; (o) 2.8 mM; (p)3.0 mM; (q) 3.2 mM; (r) 4.0 mM; (s) 6.0 mM; (t) 8.0 mM; (u) 10.0 mM; (v) 30.0 mM; (w) 50.0 mM.

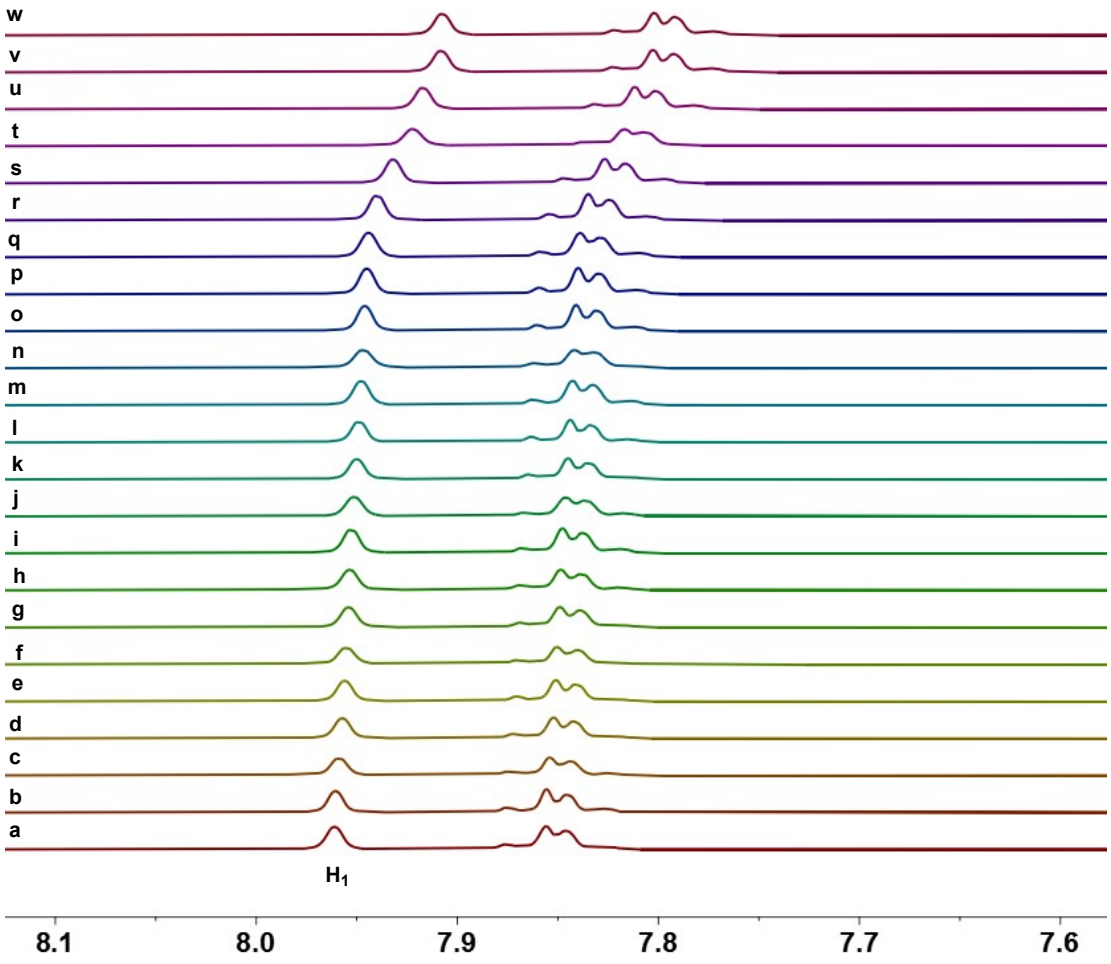


Figure S9. Zoomed in view of Figure S8

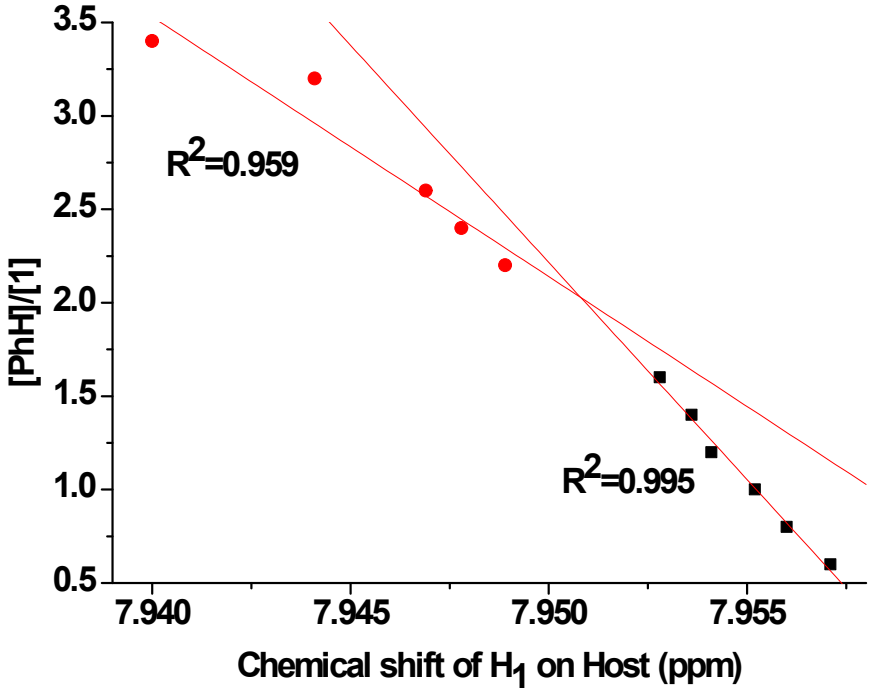


Figure S10. Mole ratio plot of the complexation of **1**and **PhH** in $CDCl_3$ at 298 K.

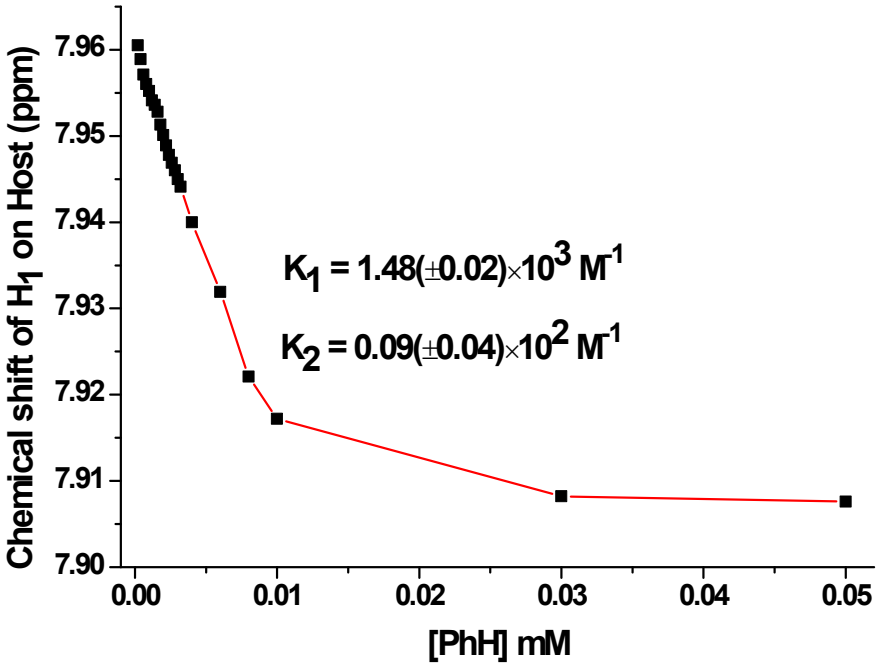


Figure S11. Plot of chemical shift (ppm) for the H_1 of **1** and **PhH** in $CDCl_3$ at 298 K.

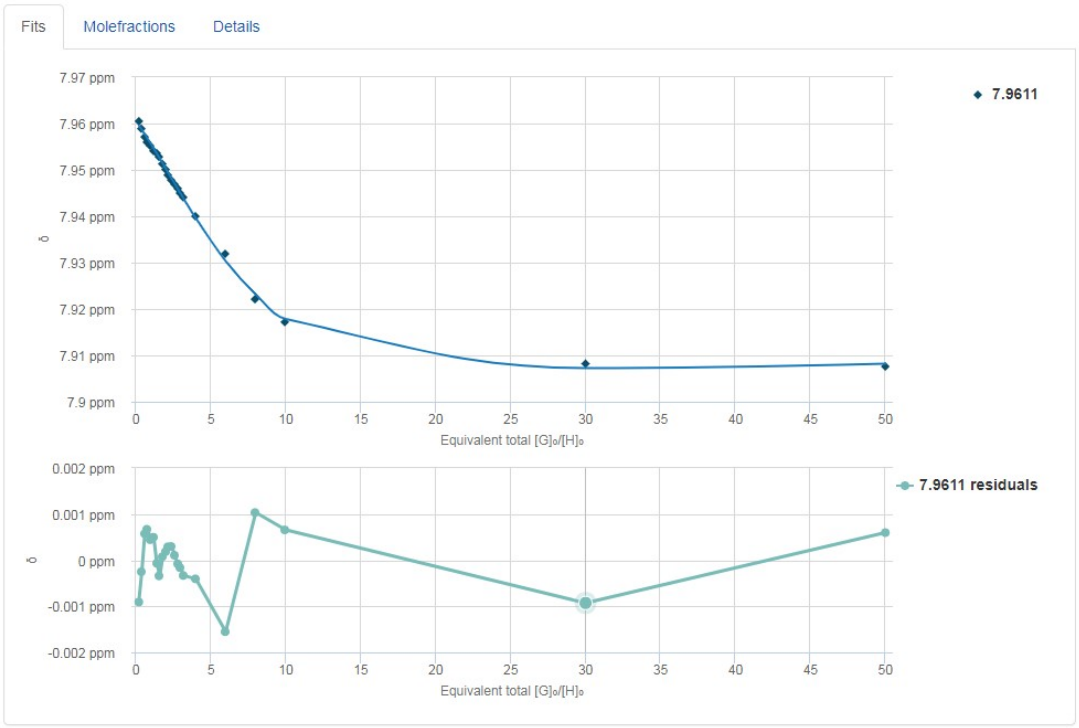


Figure S12. Screenshot of data fit for $(PhH)_2$@1

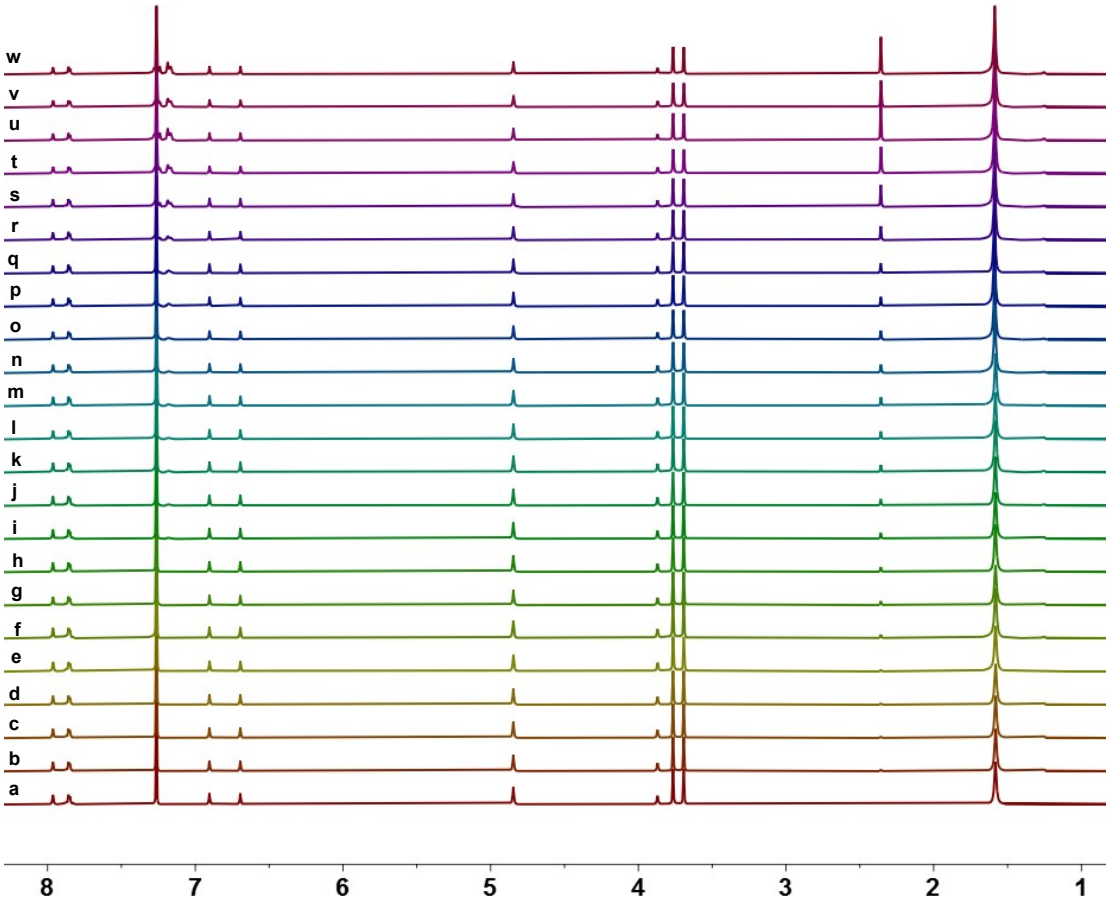


Figure S13. ^{1}H NMR spectra (400 MHz, $CDCl_3$, v/v, 298 K) of **1** at a concentration

of 1.0 mM with different concentrations of **Tol**: (a) 0.00 mM; (b) 0.2 mM; (c) 0.4 mM; (d) 0.6 mM; (e) 0.8 mM; (f) 1.0 mM; (g) 1.2 mM; (h) 1.4 mM; (i) 1.6mM; (j) 1.8 mM; (k) 2.0 mM; (l) 2.2 mM; (m) 2.4 mM; (n) 2.6 mM; (o) 2.8 mM; (p)3.0 mM; (q) 3.2 mM; (r) 4.0 mM; (s) 6.0 mM; (t) 8.0 mM; (u) 10.0 mM; (v) 30.0 mM; (w) 50.0 mM.

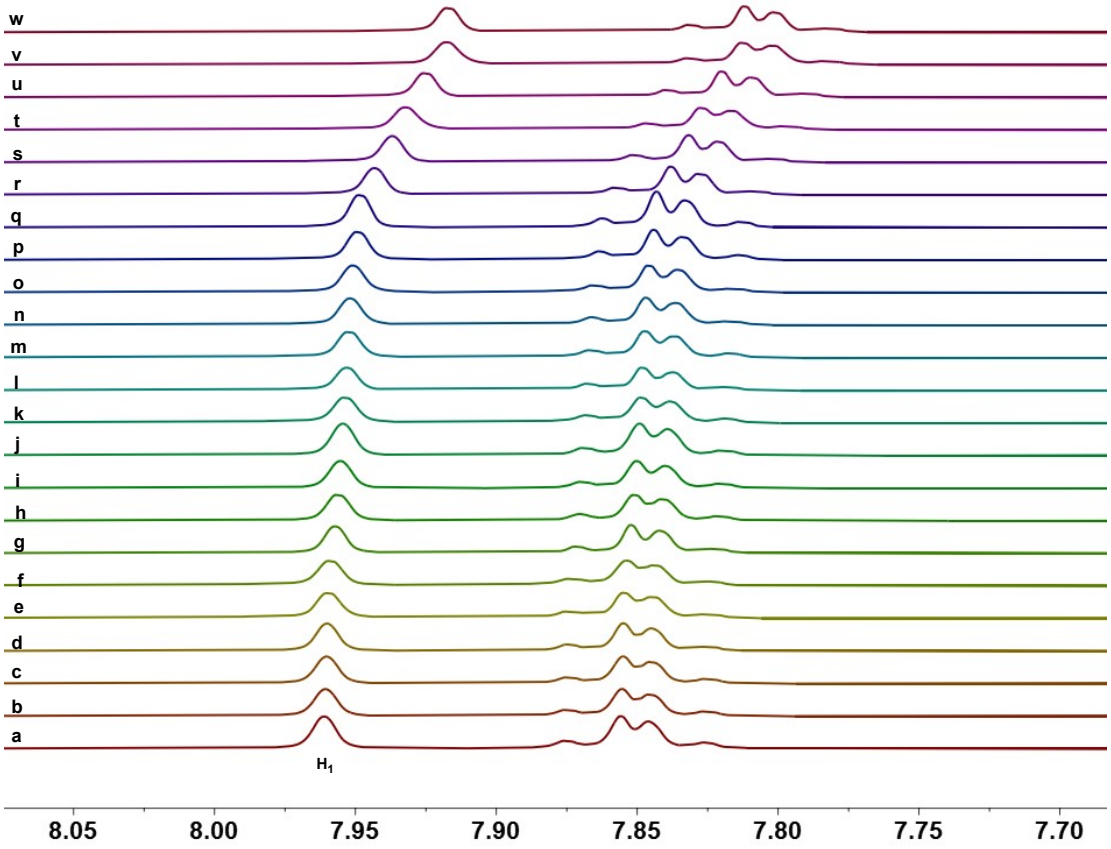


Figure S14. Zoomed in view of Figure S13

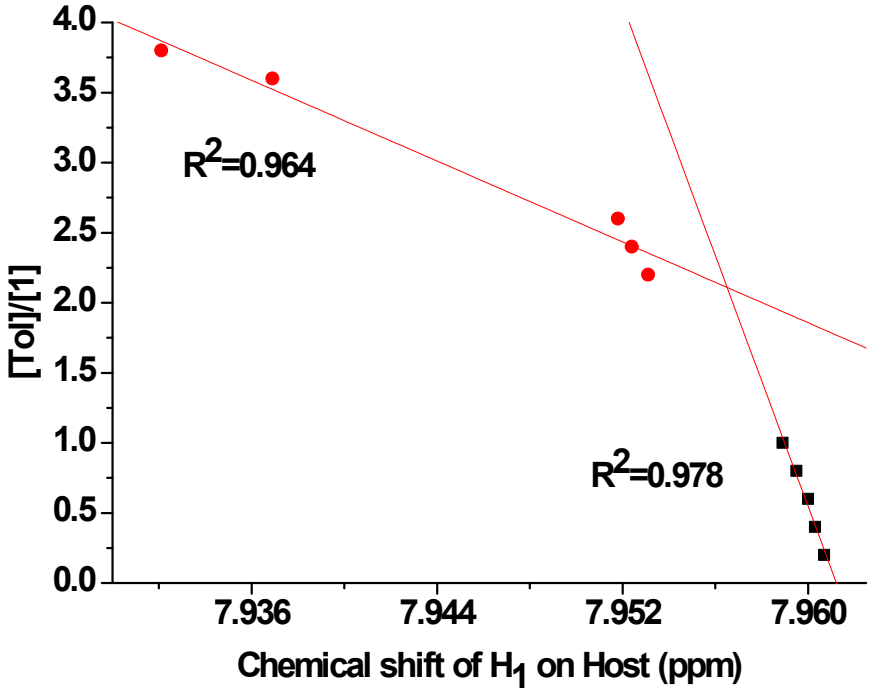


Figure S15. Mole ratio plot of the complexation of **1**and **Tol** in $CDCl_3$ at 298 K.

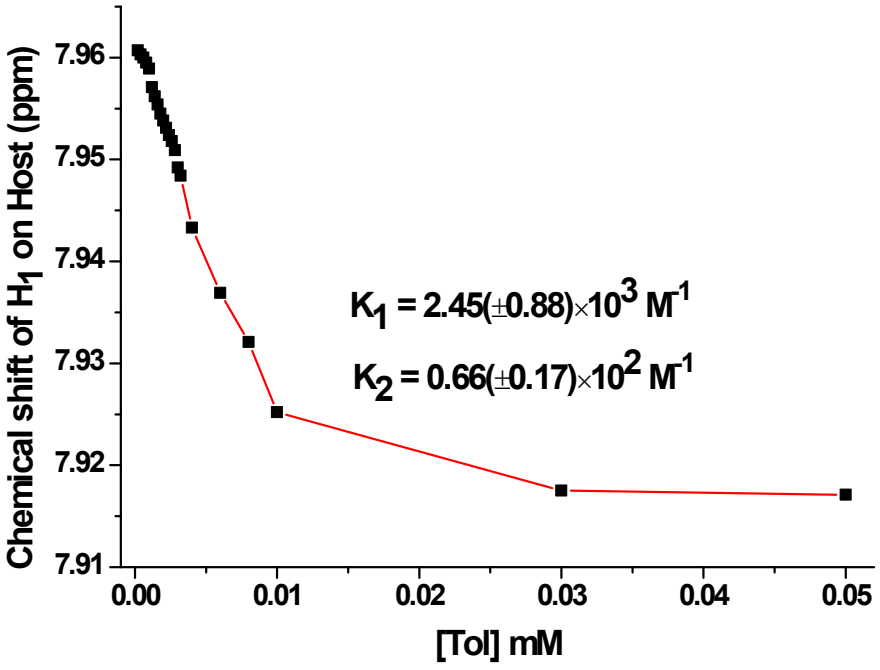


Figure S16. Plot of chemical shift (ppm) for the H_1 of **1** and **Tol** in $CDCl_3$ at 298 K.

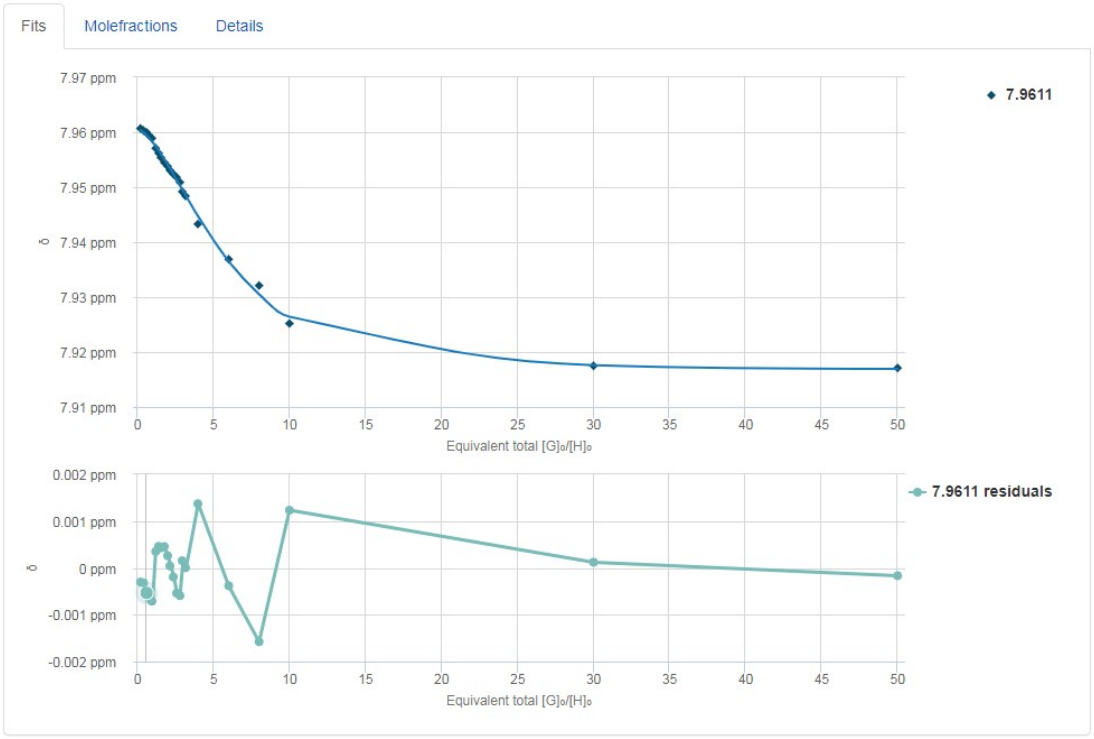


Figure S17. Screenshot of data fit for Tol_2@1