Electronic Supporting Information

Hydrogen Bonded Molecular Capsule: Probing Role of Water Molecules for Capsule Formation in a Modified Cyclotricatechylene

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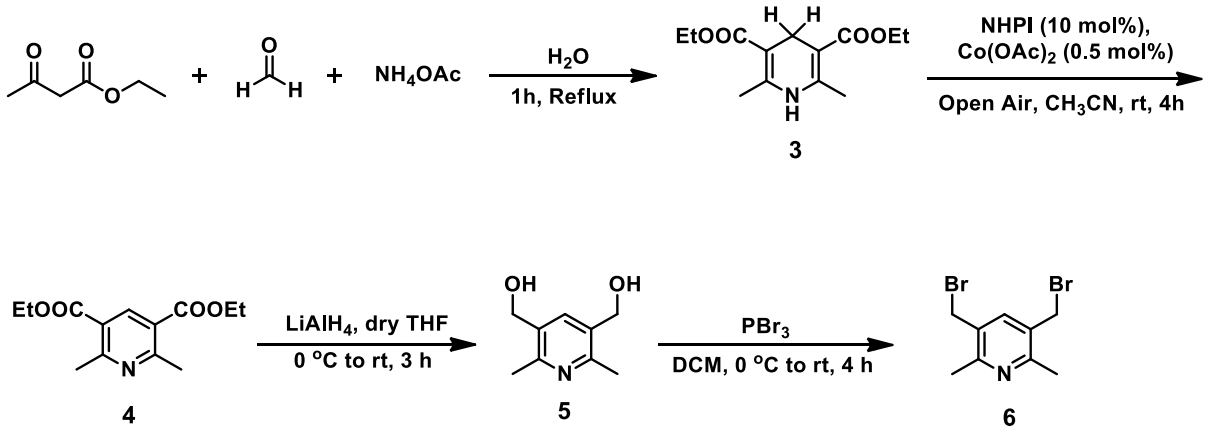
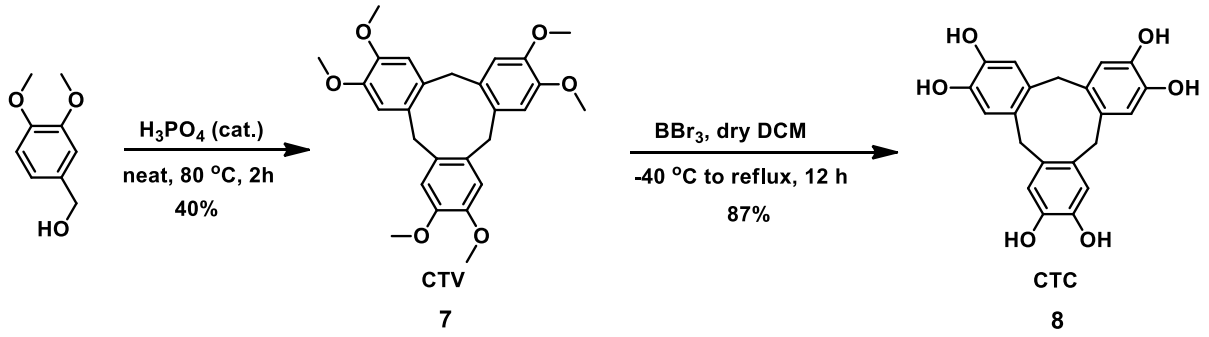
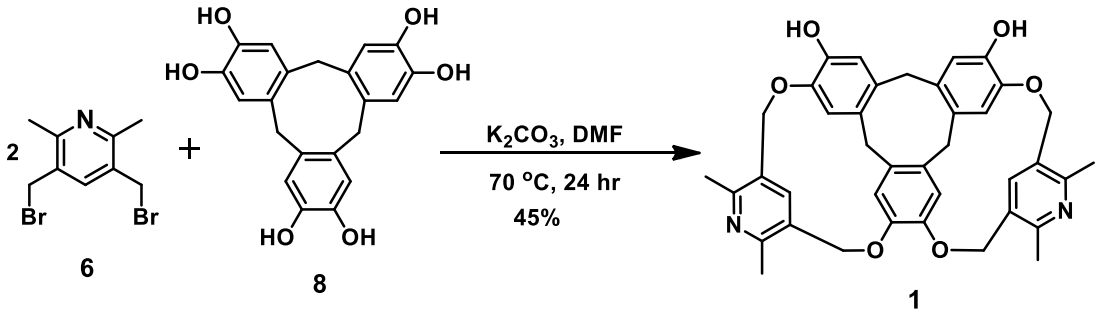
Synthetic Schemes



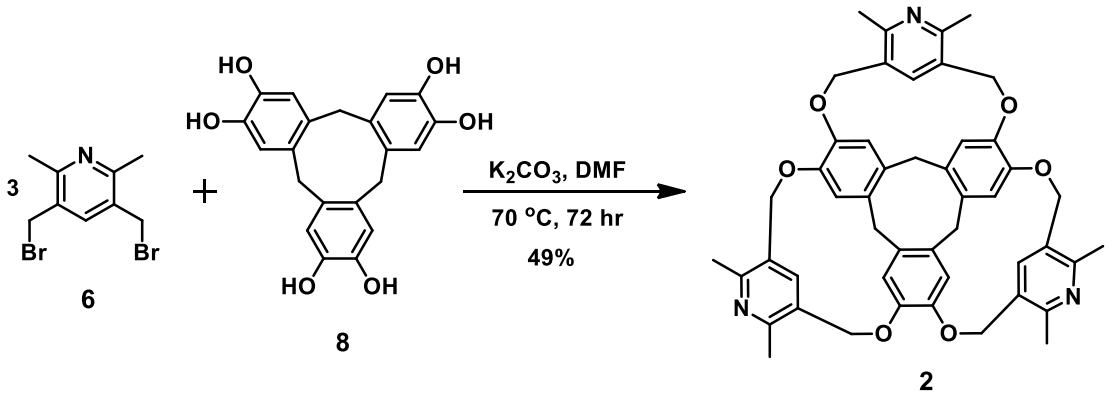
Scheme S1. Synthesis of 3,5-bis(bromomethyl)-2,6-dimethylpyridine (**6)**



Scheme S2. Synthesis of CTC (**7)**

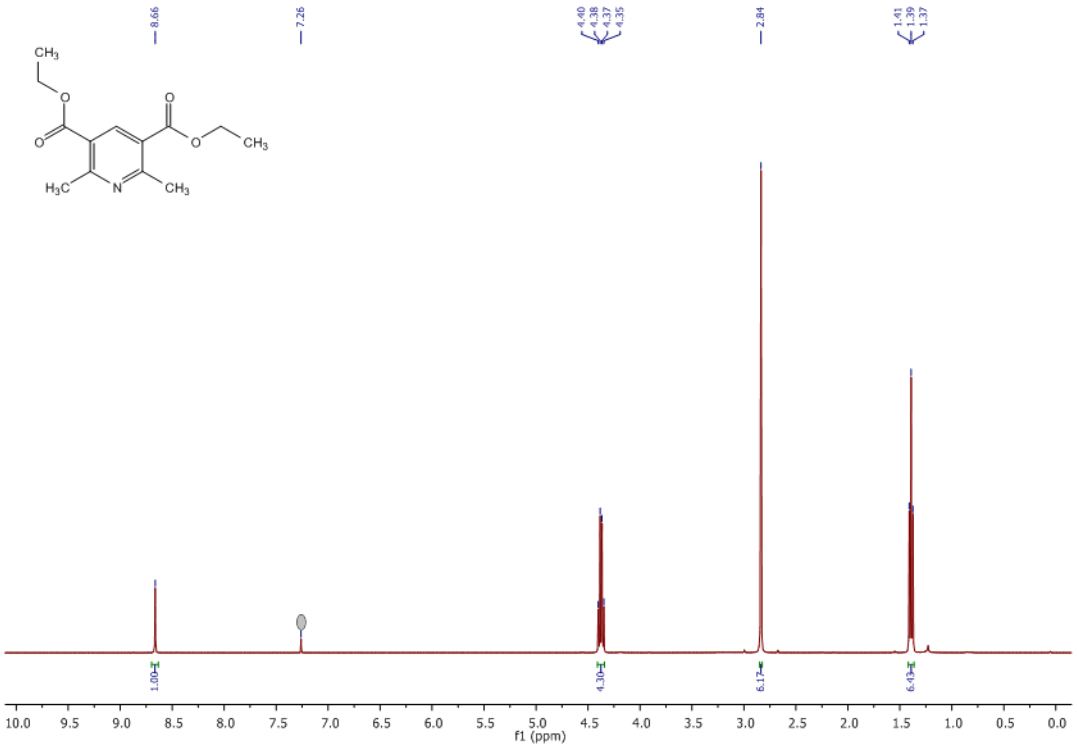


Scheme S3. Synthesis of $CTC(Py)_2(OH)_2$ (**1)**



Scheme S4. Synthesis of CTC(Py)$_3$ (**2**)

Figure S1. ^{1}H NMR and^{13}C NMR of Diethyl 2,6-dimethylpyridine-3,5-dicarboxylate (4)



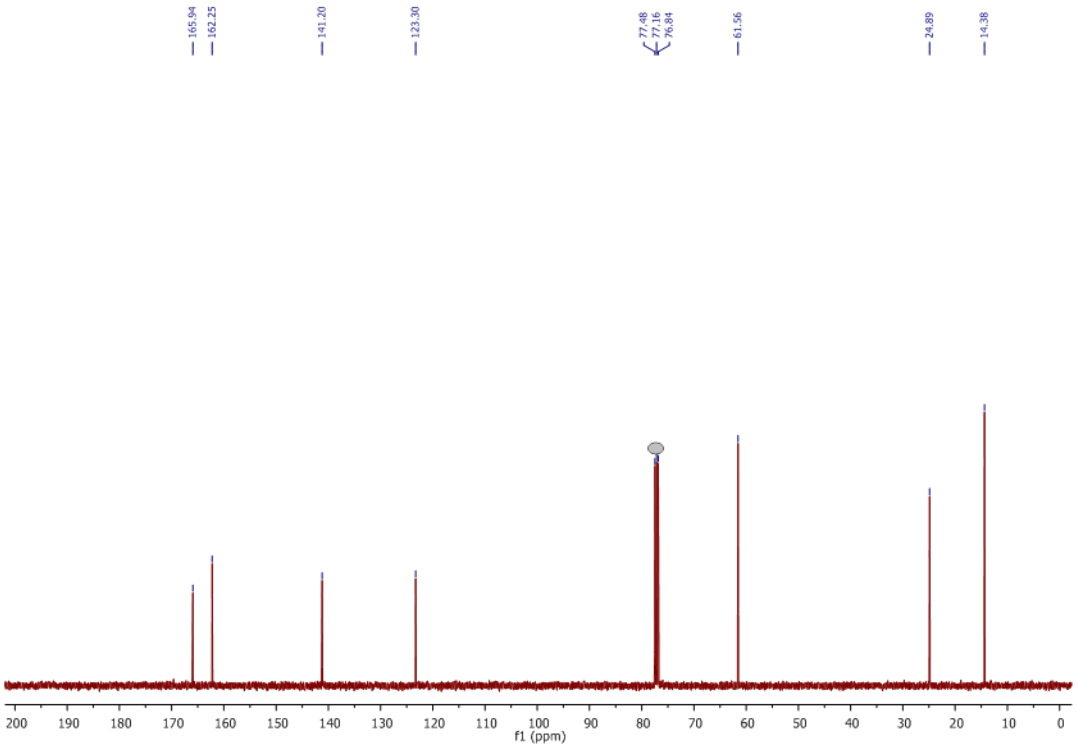
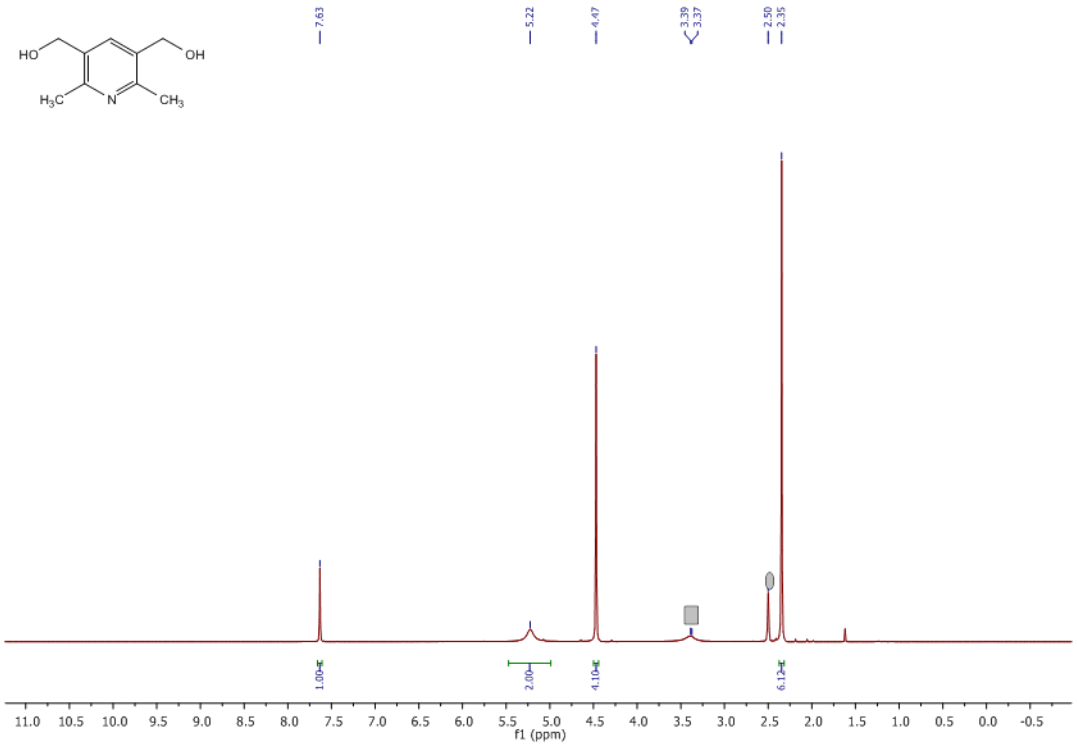


Figure S2. ^{1}H NMR and^{13}C NMR of(2,6-Dimethylpyridine-3,5-diyl)dimethanol (5)



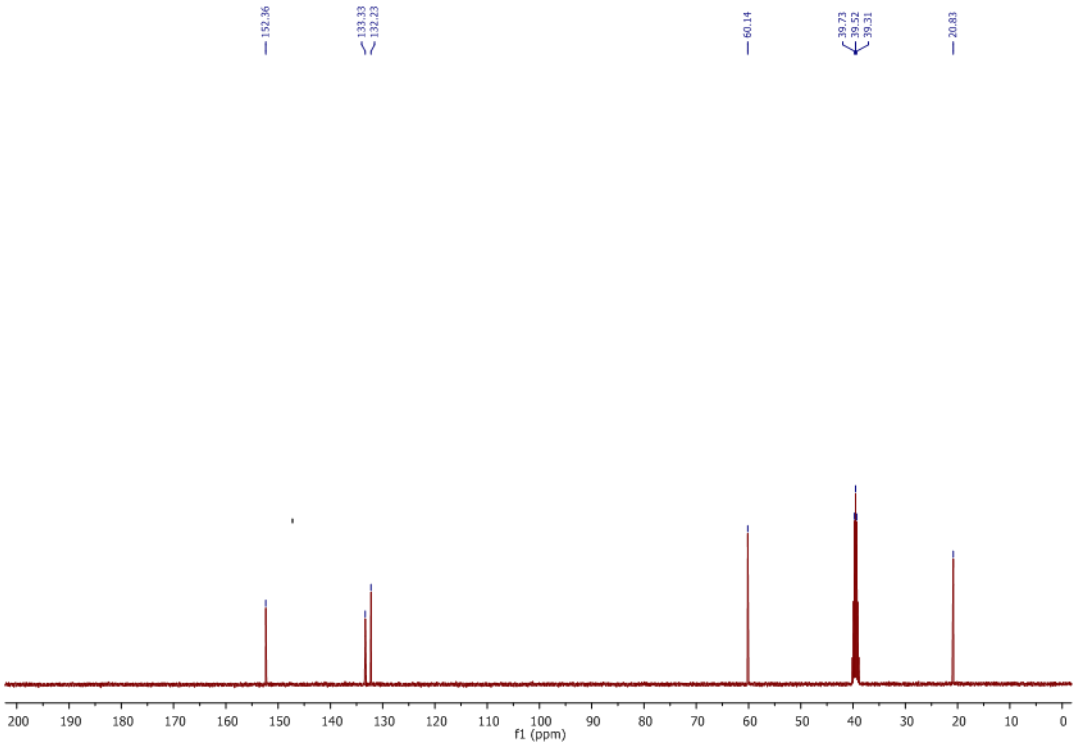


Figure S3. ^{1}H NMR and^{13}C NMR of3,5-bis(bromomethyl)-2,6-dimethylpyridine (6)

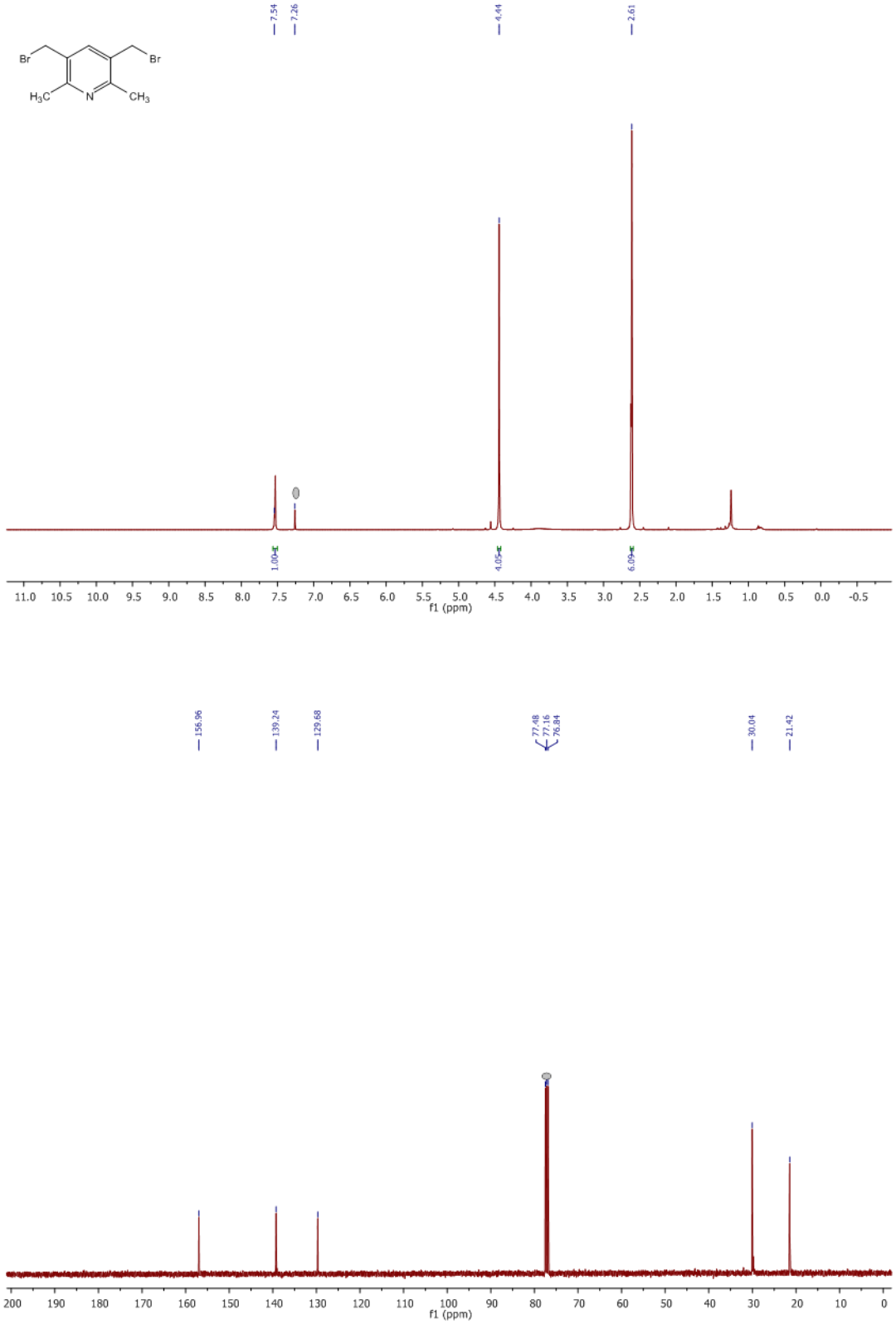


Figure S4. ^{1}H NMR and^{13}C NMR ofCyclotriveratrylene (CTV) (7)

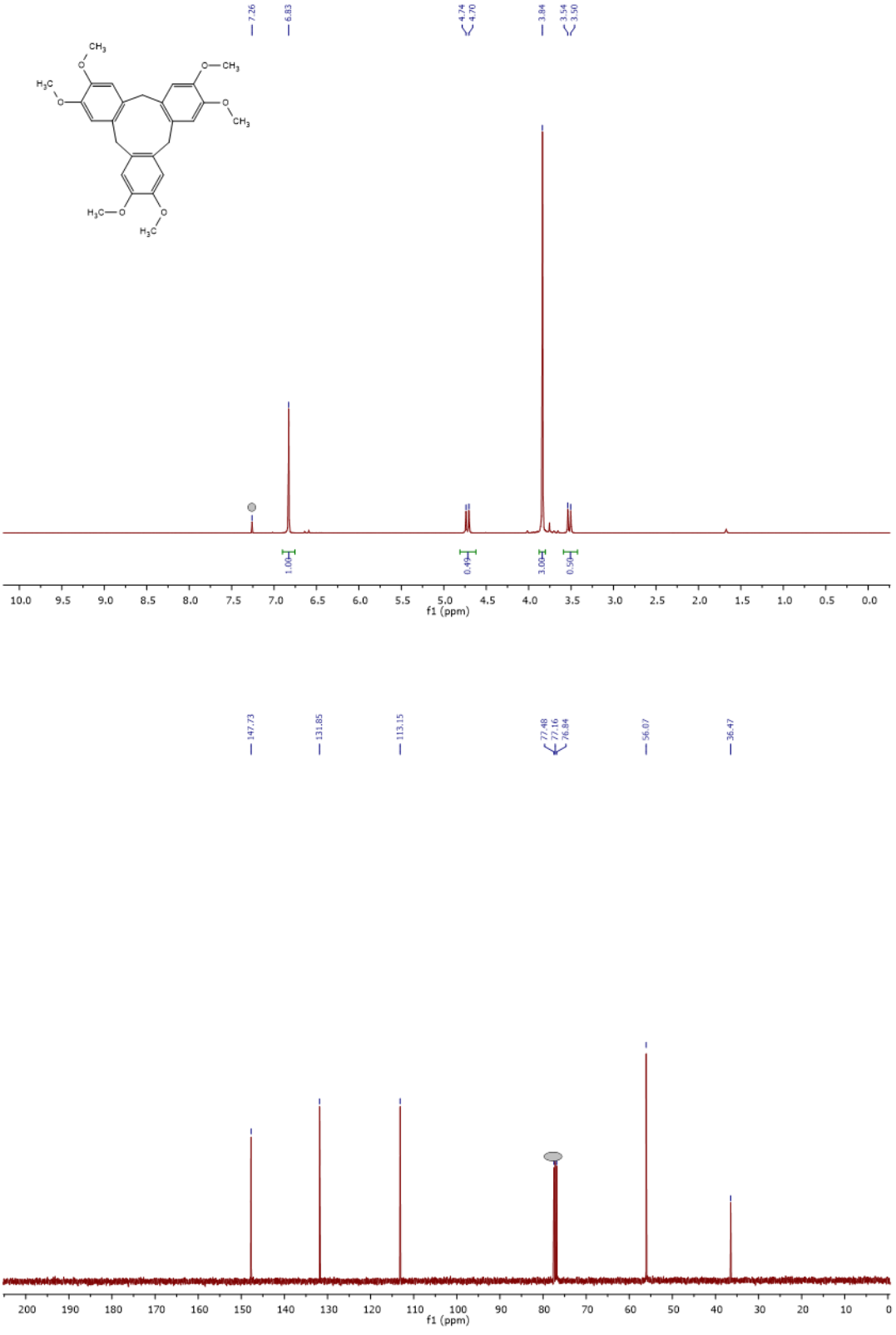


Figure S5. ^{1}H NMR and^{13}C NMR ofCyclotricatechylene (CTC) (8)

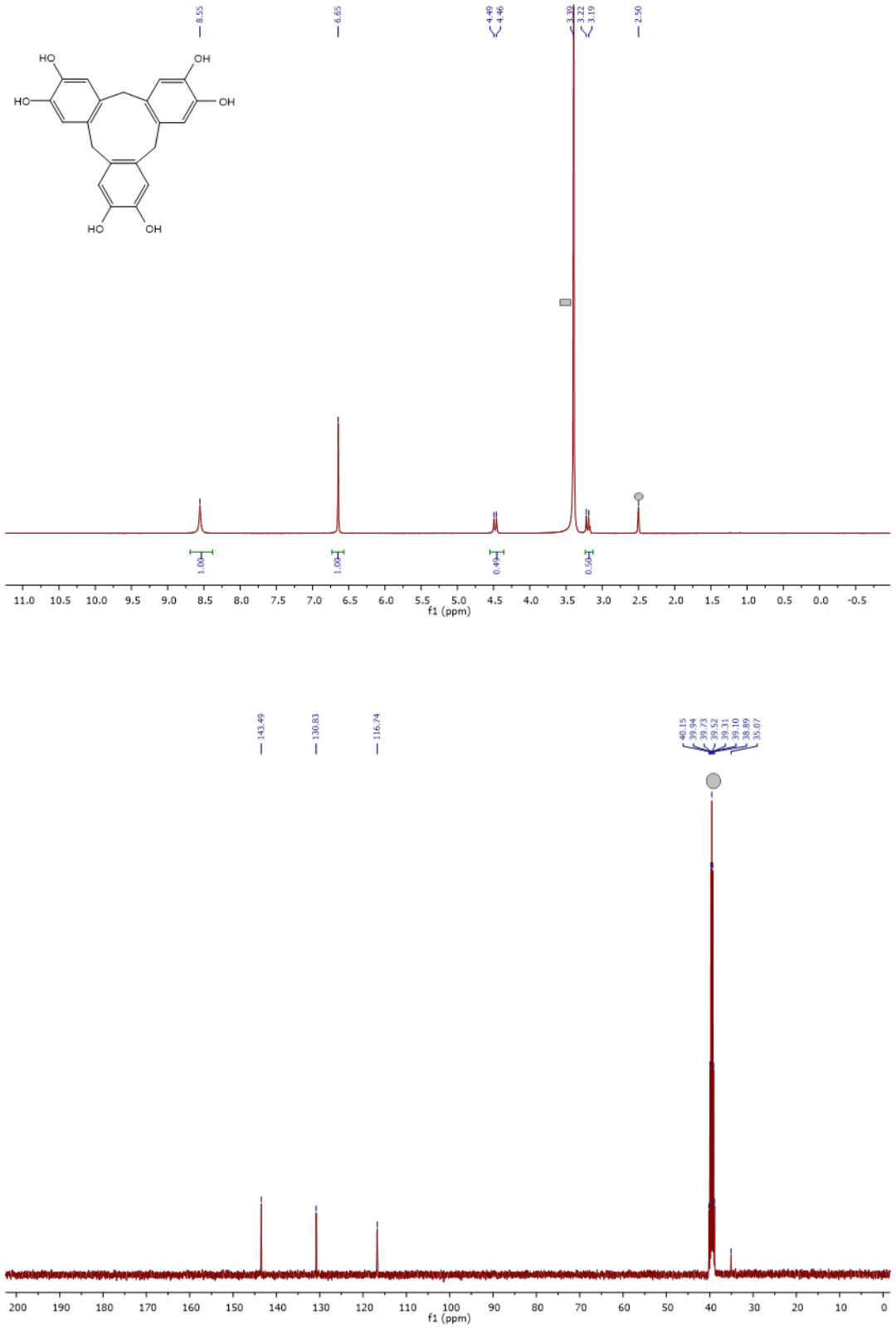
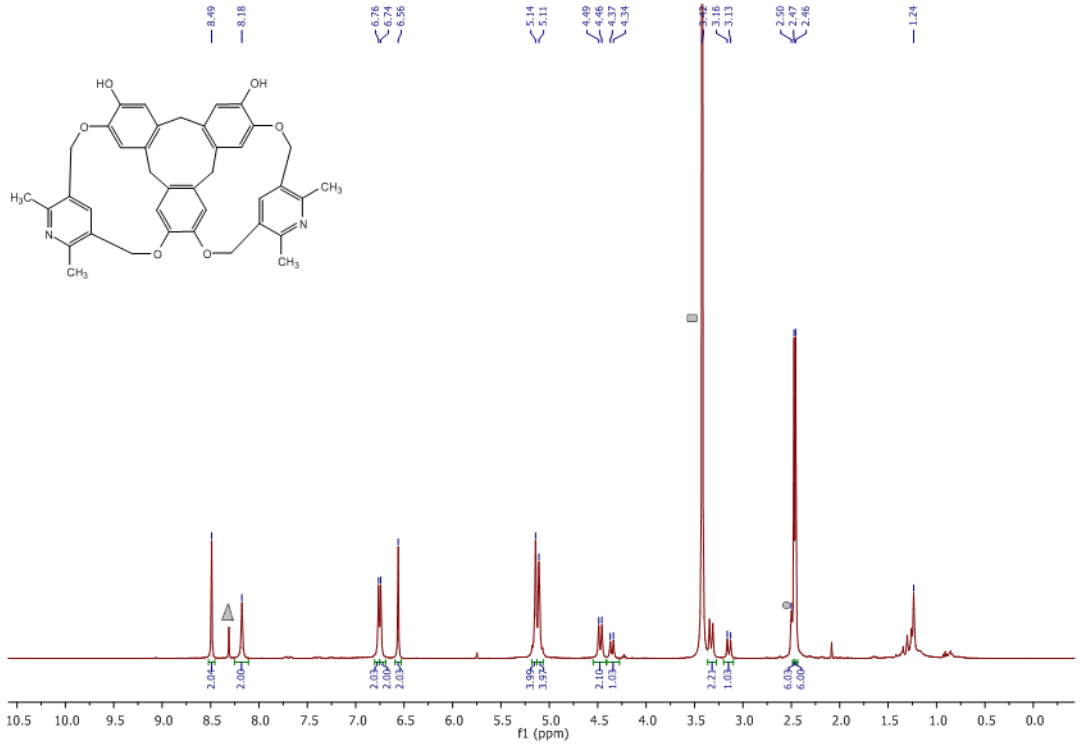


Figure S6. ^{1}H NMR and^{13}C NMR of$(CTC(Py)_2(OH)_2)$ (1)



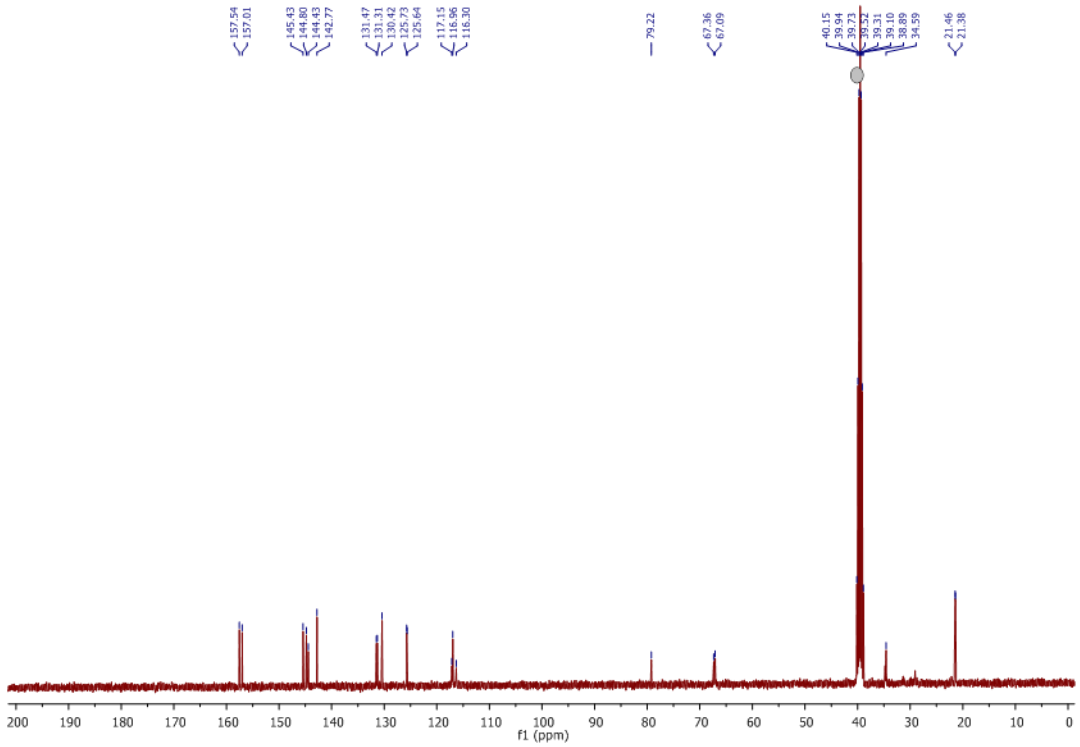


Figure S7. ^{1}H NMR and^{13}C NMR of(CTC(Py)$_3$) (2)

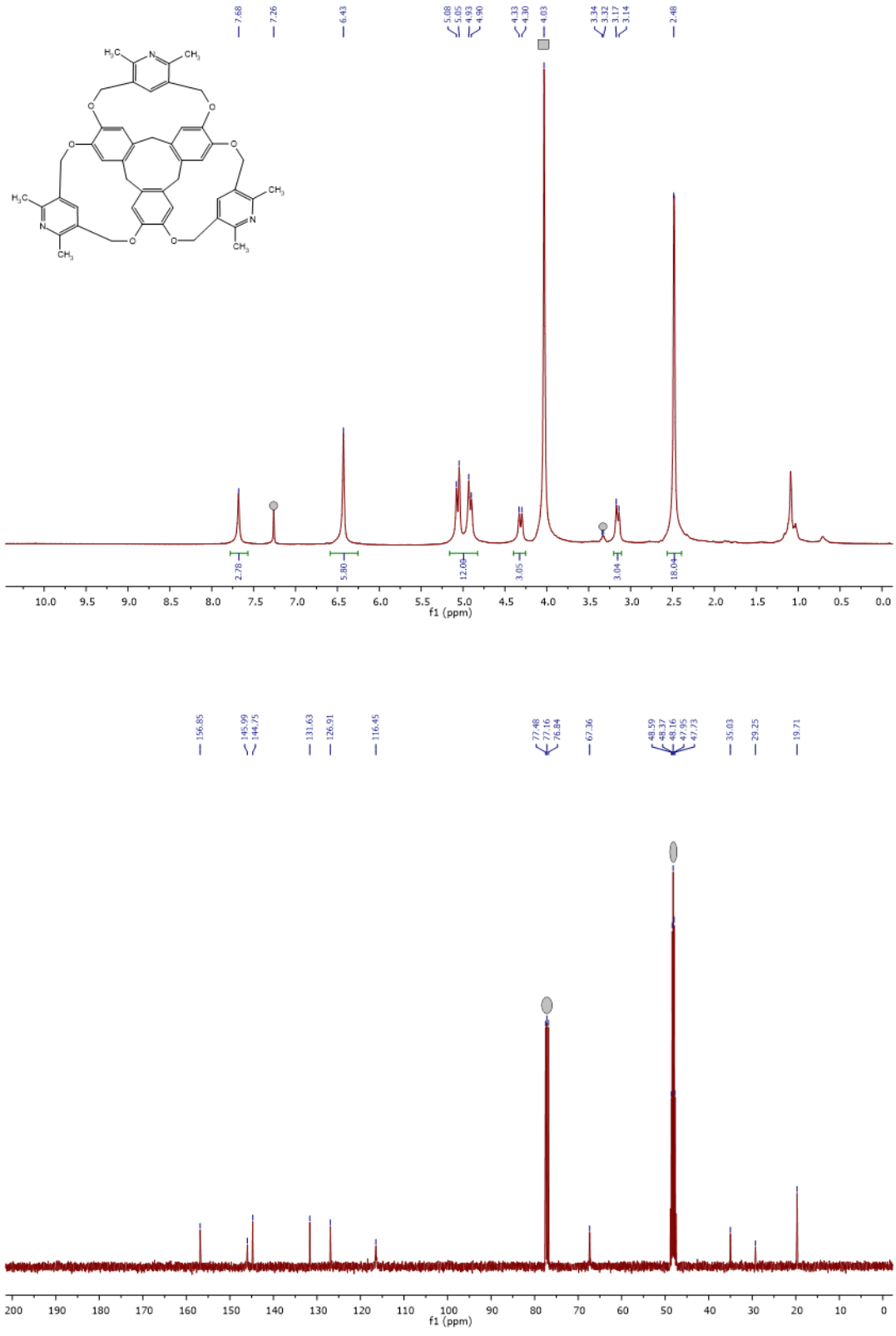


Figure S8. ESI-MS spectrum of CTC(Py)$_2$(OH)$_2$(1)

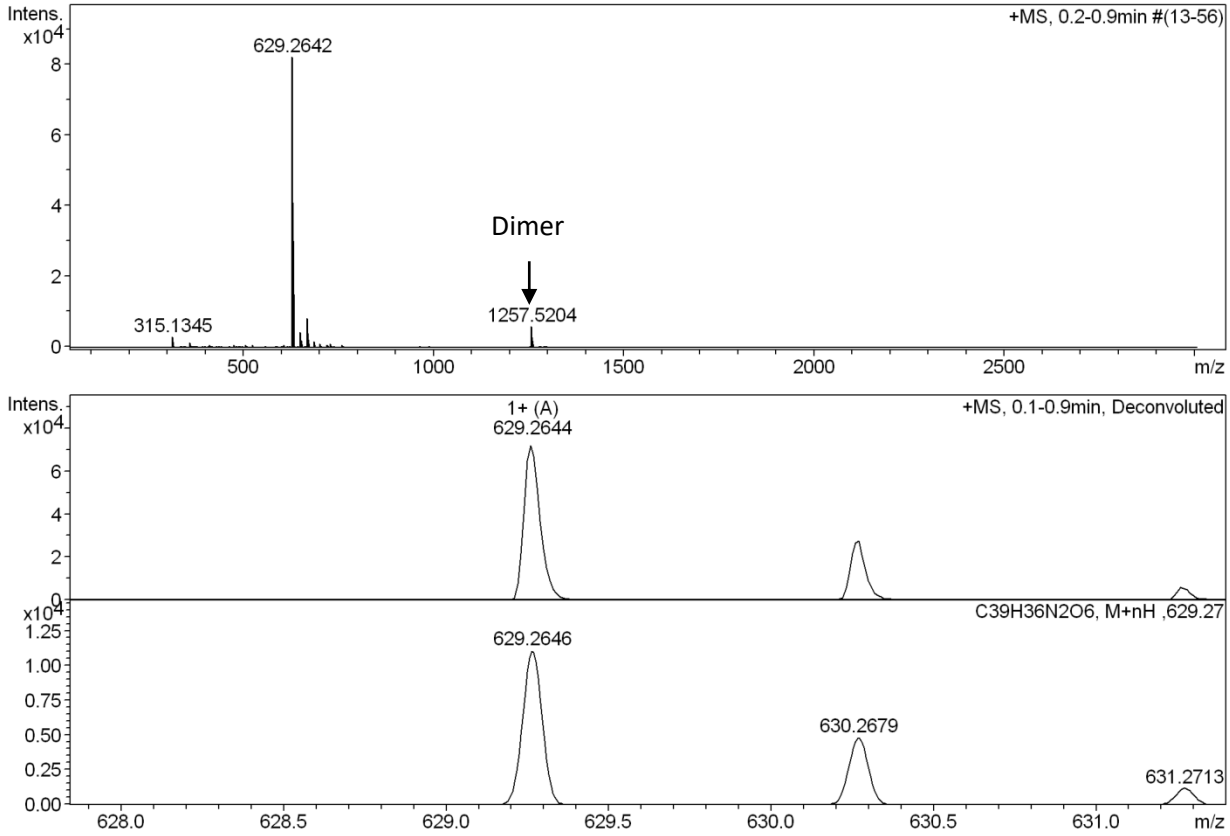
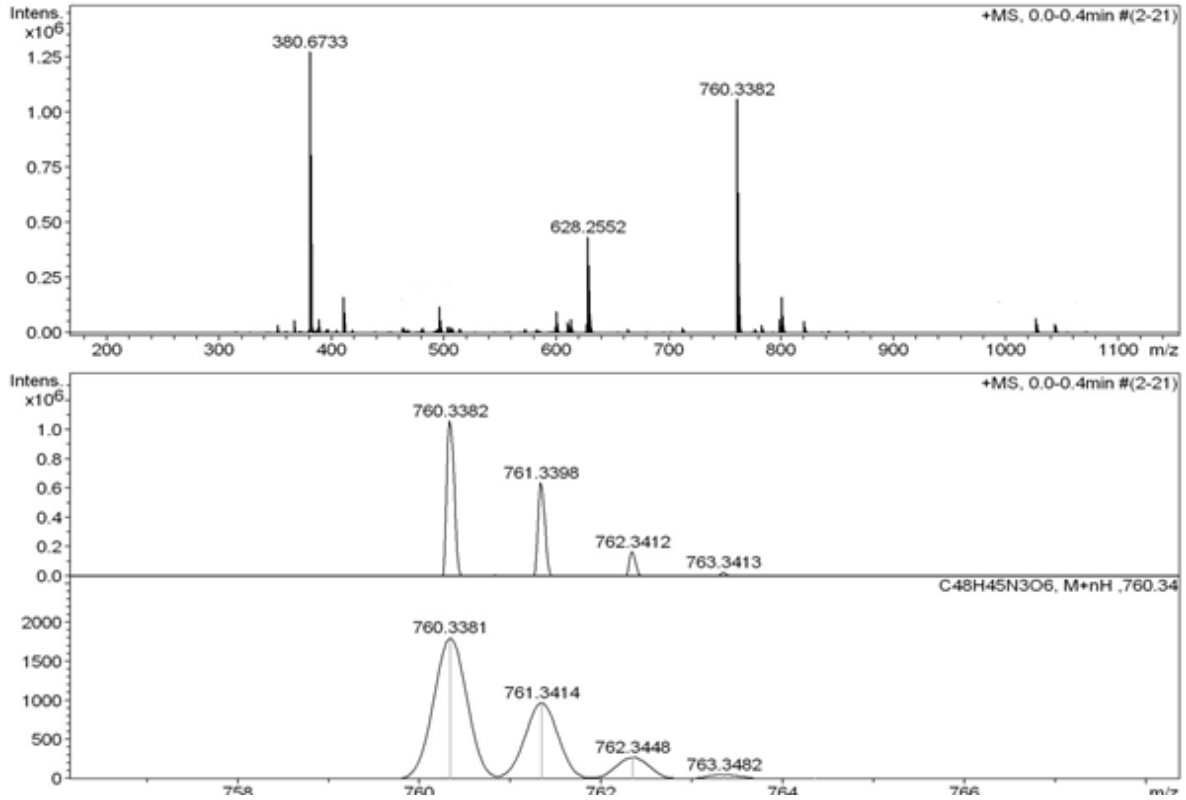


Figure S9. ESI-MS spectrum of CTC(Py)$_3$(2)



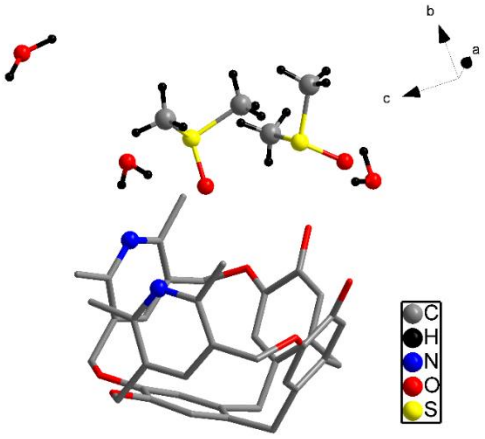


Figure S10. Asymmetric unit of **1**. Hydrogen atoms of **1** have been deleted for clarity.

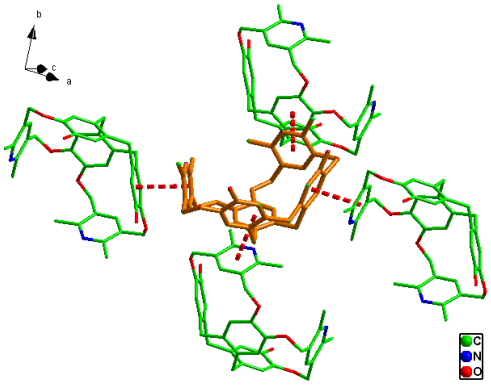


Figure S11. Arrangement of four monomers around a central molecule of **1**, mediated by π–π stacking (shown in red broken bonds). H atoms and solvent molecules have been omitted for clarity.

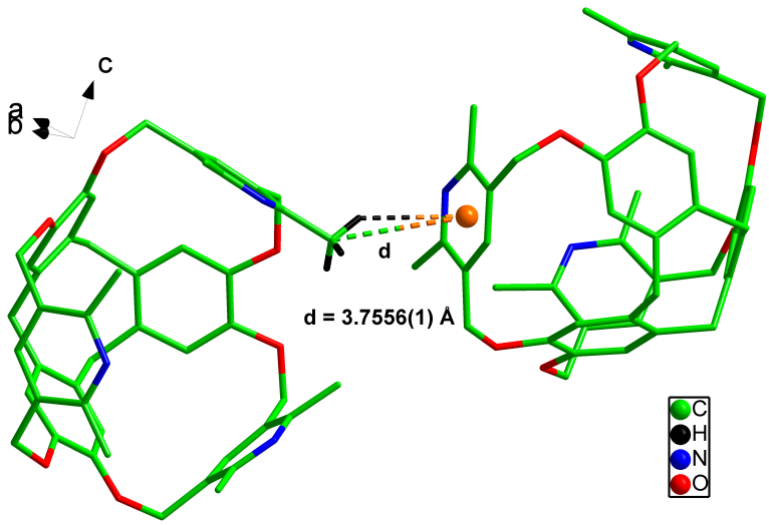


Figure S12. CH-π interaction between pyridine methyl groups of one molecule of **2**, with pyridine ring of another. C and H interactions with centroid (orange in colour) of aromatic ring are shown in broken bonds. Rest hydrogen atoms and solvent molecules have been omitted for clarity.

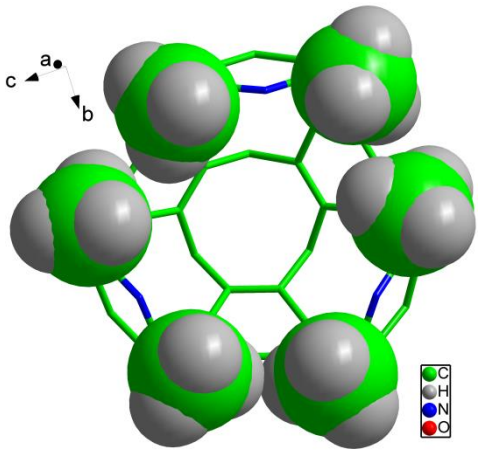


Figure S13. Steric hindrance between methyl groups (shown in space fill model) of adjacent pyridine bridges in **2**. Non-methyl H atoms and water molecules have been removed for clarity.

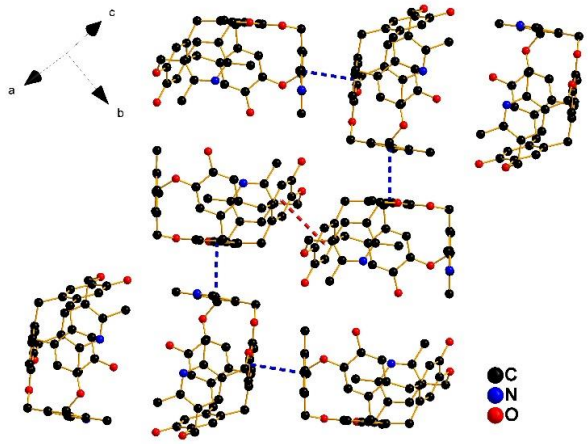


Figure S14: π -π stacking interactions among monomer **1** capsular assembly. Hydrogen atoms and DMSO has been omitted for clarity.

Table 1. Crystal data and structure refinement for **CTC(Py)$_2$(OH)$_2$(1)**forming capsular assembly.

Identification code	CTC-2Py	
Empirical formula	C42.60 H52.80 N2 O10.52 S1.80	
Formula weight	818.89	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P $2_{1/n}$	
Unit cell dimensions	a = 16.8196(7) Å	α= 90°.
	b = 14.4225(5) Å	β= 99.568(3)°.
	c = 17.2295(8) Å	γ = 90°.
Volume	4121.4(3) Å^3	
Z	4	
Density (calculated)	1.320 Mg/m^3	
Absorption coefficient	0.181 mm^{-1}	
F(000)	1741	
Crystal size	0.27 x 0.22 x 0.12 mm^3	
Theta range for data collection	2.825 to 26.019°.	
Index ranges	-20<=h<=16, -17<=k<=17, -21<=l<=20	
Reflections collected	22935	
Independent reflections	8104 [R(int) = 0.0368]	
Completeness to theta = 25.242°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8104 / 25 / 588	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0736, wR2 = 0.2154	
R indices (all data)	R1 = 0.1042, wR2 = 0.2409	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.088 and -0.638 e.Å^{-3}	
CCDC	1525712	

Table 2. Hydrogen bonds for **CTC(Py)$_2$(OH)$_2$ (1)** [Å and °].(Capsular assembly)

D-H...A	d(D-H)	d(H...A)	d(D...A)	Angle(DHA)
O(5)-H(5)...O(10)	0.87	1.83	2.672(4)	161.5
O(10)-H(10A)...O(7)	1.01(2)	1.83(4)	2.750(4)	151(6)
O(6)-H(6)...O(11)#2	0.86(5)	1.86(5)	2.692(4)	164(4)
O(11)-H(11A)...N(2)	0.93(5)	1.91(5)	2.803(4)	159(4)
O(11)-H(11B)...O(7)#2	0.98(2)	1.83(3)	2.765(4)	159(5)
O(10)-H(10B)...N(1)#2	1.00(2)	1.89(4)	2.863(4)	162(8)

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+1/2,z+1/2 #2 -x+1,-y+1,-z+1 #3 x-1/2,-y+3/2,z-1/2 #4 x+1/2,-y+3/2,z+1/2

Table 3. Crystal data and structure refinement for **CTC(Py)$_2$(OH)$_2$(1)** forming non-capsular assembly.

Identification code	CTC-2Py-linear	
Empirical formula	C45 H36 N2 O10 S3	
Formula weight	860	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1/c	
Unit cell dimensions	a = 12.3804(5) Å	α= 90°.
	b = 25.0918(8) Å	β= 110.287°.
	c = 15.6377(5) Å	γ = 90°.
Volume	4556.5(3) Å^3	
Z	4	
Density (calculated)	1.2 Mg/m^3	
Absorption coefficient	0.219 mm^{-1}	
F(000)	1752	
Crystal size	0.24 x 0.22 x 0.21 mm^3	

Theta range for data collection	1.754 to 29.460°.
Index ranges	-17<=h<=16, -34<=k<=34, -21<=l<=21
Reflections collected	71938
Independent reflections	12641 [R_{int} = 0.0357, R_{sigma} = 0.0263]
Completeness to theta = 25.242°	99.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12641 / 0 / 577
Goodness-of-fit on F^2	1.097
Final R indices [I>2sigma(I)]	R_1 = 0.0720, wR_2 = 0.2274
R indices (all data)	R_1 = 0.1003, wR_2 = 0.2480
Largest diff. peak and hole	0.748 and -0.507 e.Å^{-3}
CCDC	1530352

Table 4. Hydrogen bonds for CTC-Py2 [Å and °].(non-capsular assembly)

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(11)-H(11B)...O(5)#1	0.97	2.46	3.428(4)	178.7
C(18)-H(18)...O(14)#2	0.93	2.58	3.439(8)	153.3
C(21)-H(21)...O(14)#2	0.93	2.54	3.371(6)	148.7
C(29)-H(29A)...O(11)#3	0.97	2.48	3.446(5)	176.9
C(30)-H(30B)...O(12)	0.96	2.64	3.109(6)	110.8
C(31)-H(31A)...O(4)	0.96	2.58	3.194(6)	122.0
C(31)-H(31A)...O(10)#3	0.96	2.57	3.475(6)	156.7
C(41)-H(41A)...O(11)	0.96	2.54	3.164(6)	122.4
C(42)-H(42A)...O(3)	0.96	2.44	3.117(5)	127.5
C(46)-H(46A)...O(5)	0.96	2.52	3.149(6)	122.7
C(66)-H(66)...O(15)	1.04	2.58	3.484(8)	144.7
C(68)-H(68)...O(15)	0.93	2.48	3.296(6)	147.0
C(76)-H(76A)...O(9)	0.96	2.48	3.142(6)	125.9
C(76)-H(76B)...S(4)	0.96	2.99	3.704(6)	132.0
C(80)-H(80A)...O(6)	0.96	2.49	3.166(6)	127.3
C(80)-H(80C)...O(9)#4	0.96	2.62	3.385(6)	137.2
O(1)-H(1O)...N(3)	0.82	2.09	2.764(4)	139.1
O(2)-H(2O)...N(1)	0.82	2.04	2.707(4)	137.7
O(7)-H(7O)...N(4)#2	0.82	2.10	2.777(4)	140.4
O(8)-H(8O)...N(2)#2	0.82	2.04	2.741(4)	143.6

Table 5. Crystal data and structure refinement for **CTC(Py)$_3$(2)**.

Identification code	CTC-3Py	
Empirical formula	C48 H45 N3 O6	
Formula weight	759.87	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P n a 21	
Unit cell dimensions	a = 20.6343(7) Å	α= 90°
	b = 20.0381(7) Å	β= 90°
	c = 12.2555(4) Å	γ = 90°
Volume	5067.3(3) Å^3	
Z	4	
Density (calculated)	0.996 Mg/m^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	1608.0	
Crystal size	0.28 x 0.21 x 0.15 mm^3	
Theta range for data collection	1.948 to 27.615°.	
Index ranges	-26<=h<=26, -26<=k<=25, -11<=l<=15	
Reflections collected	71022	
Independent reflections	9985 [R(int) = 0.0993]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9985 / 1 / 520	
Goodness-of-fit on F^2	0.975	
Final R indices [I>2sigma(I)]	R_1 = 0.0494, wR_2 = 0.0875	
R indices (all data)	R_1 = 0.1010, wR_2 = 0.0962	
Largest diff. peak and hole	0.12 and -0.121 e.Å^{-3}	
CCDC	1525713	