Efficient synthesis of porous triazine-based macrocycles with 22-carbon and 6-nitrogen ring atoms and their adsorption/desorption of non-volatile organic compounds

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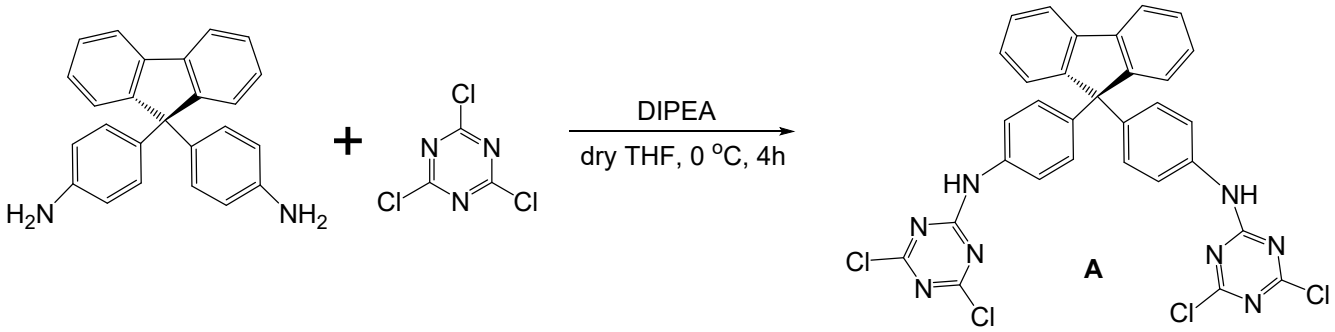
Supporting information

Experimental section

Materials and general methods: Reagents were used as received without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AMX-300 solution NMR spectrometers. Elemental analyses were carried out using an Elementar UNICUBE analyzer. Thermogravimetric analyses were performed under nitrogen with a Perkin-Elmer TGA-7 TG analyzer. Brunauer-Emmett-Teller (BET) analyses were examined with a Micrometrics TriStar II Plus system using nitrogen as the adsorbate at 77 K and carbon dioxide as the adsorbate at 195 K. All gases used were of 99.9995% purity. Crystallographic analyses were performed by Bruker D8 Venture diffractometer. HRMS were obtained from Bruker Autoflex speed MALDI-TOFMS, Bruker Compact ESI -QTOF-MS

Crystallographic determination: A suitable single crystal of **2a** or **2a▪1THF▪MeOH** was mounted on the tip of a glass fiber with dimensions of 0.11 x 0.04 x 0.02 mm3 and then placed onto the goniometer head for indexing; the intensity data collection using a Bruker D8 Venture diffractometer was equipped with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å). Collection of intensity data was conducted at 200 K. Empirical absorptions were applied using the multi-scan method. The structure was solved by direct methods and refined against F2 by the full-matrix least-squares technique using the SHELX-97 software packages.[1]

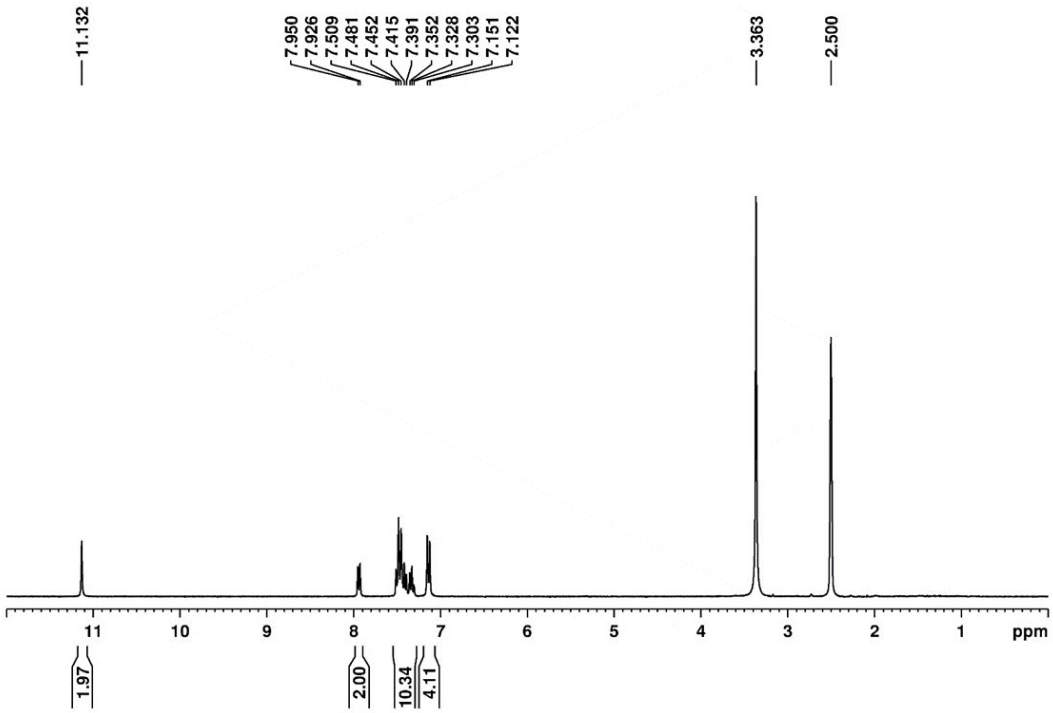
Synthesis of intermediate A



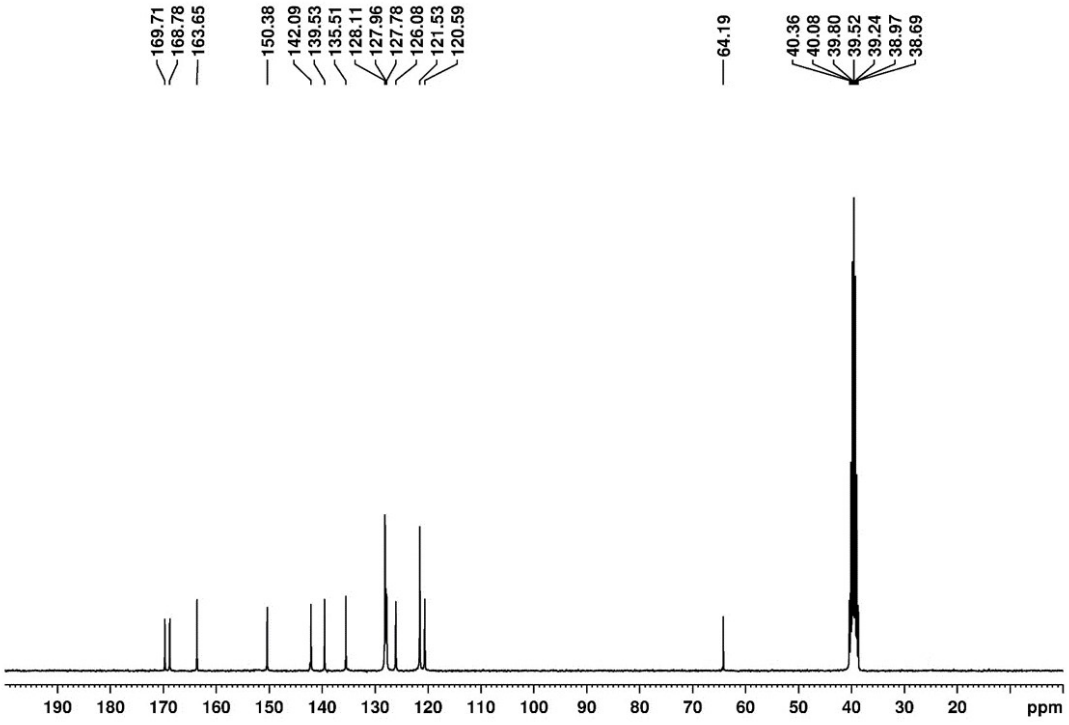
9,9-Bis(4-aminophenyl)fluorene (1.74 g, 5.0 mmol) and N,N-diisopropyl-ethylamine (1.55 g, 12.0 mmol) in dry THF (20 mL) were gradually added to cyanuric chloride (1.85 g, 10.0 mmol) in dry THF (30 mL) at 5 °C and then stirred for 4hr. After the reaction (confirmed by TLC), solvent was removed at reduced pressure to yield a solid, which was further purified by chromatography (SiO_2: 20 x 2.2 cm, eluates: THF-hexane [1:2]) and then recrystallized by CH_2Cl_2-hexane (1:1), giving intermediate **A** in 87%

(2.80 g). ^{1}H NMR (300 MHz, DMSO-D_6, 25 °C, TMS): δ 7.13 (d, *J*=8.7, 4H, 4×Ar-H), 7.30-7.50 (m, 10H, 10×Ar-H), 7.93 (d, *J*=7.2, 2H, 2×Ar-H), 11.13 (s, 2H, 2×NH) ppm. ^{13}C NMR (75 MHz, DMSO-D_6, 25 °C, TMS): δ 64.19, 120.59, 121.53, 126.08, 127.78, 127.96, 128.11, 135.51, 139.53, 142.09, 150.38, 163.65, 168.78, 169.71 ppm. MS cacld for $C_{31}H_{18}Cl_4N_8$ $[M]^+$: 644.3; found 644.4.

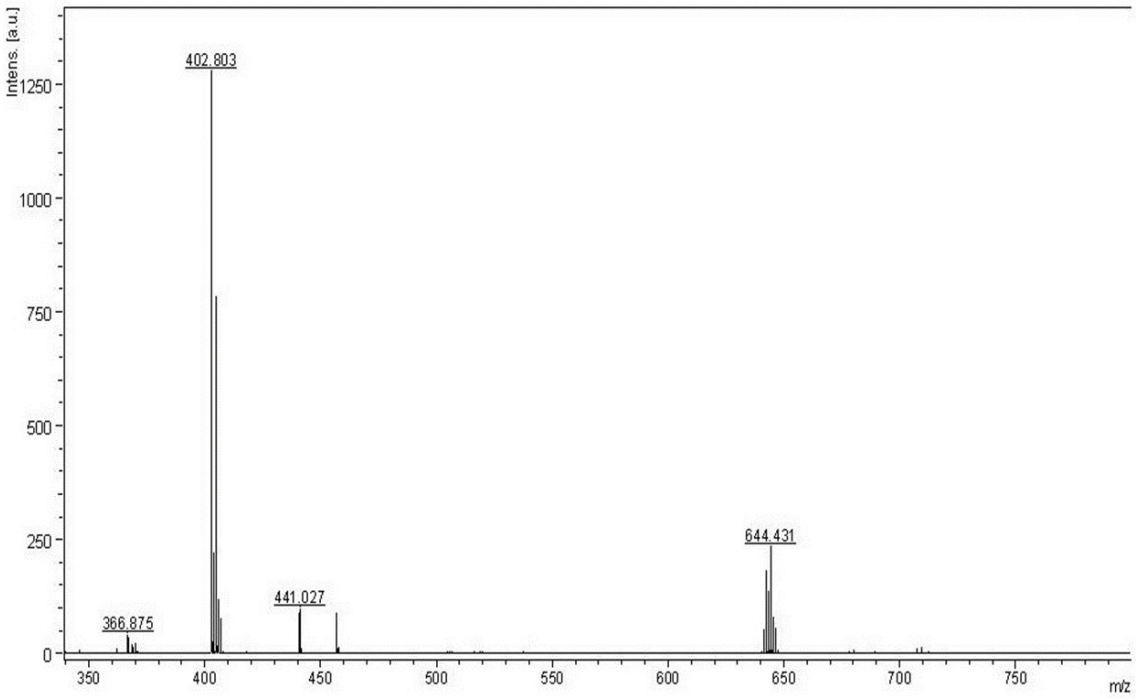
^{1}H NMR of **A**



^{13}C NMR of **A**



mass spectra of **A**


Intens. [a.u.]
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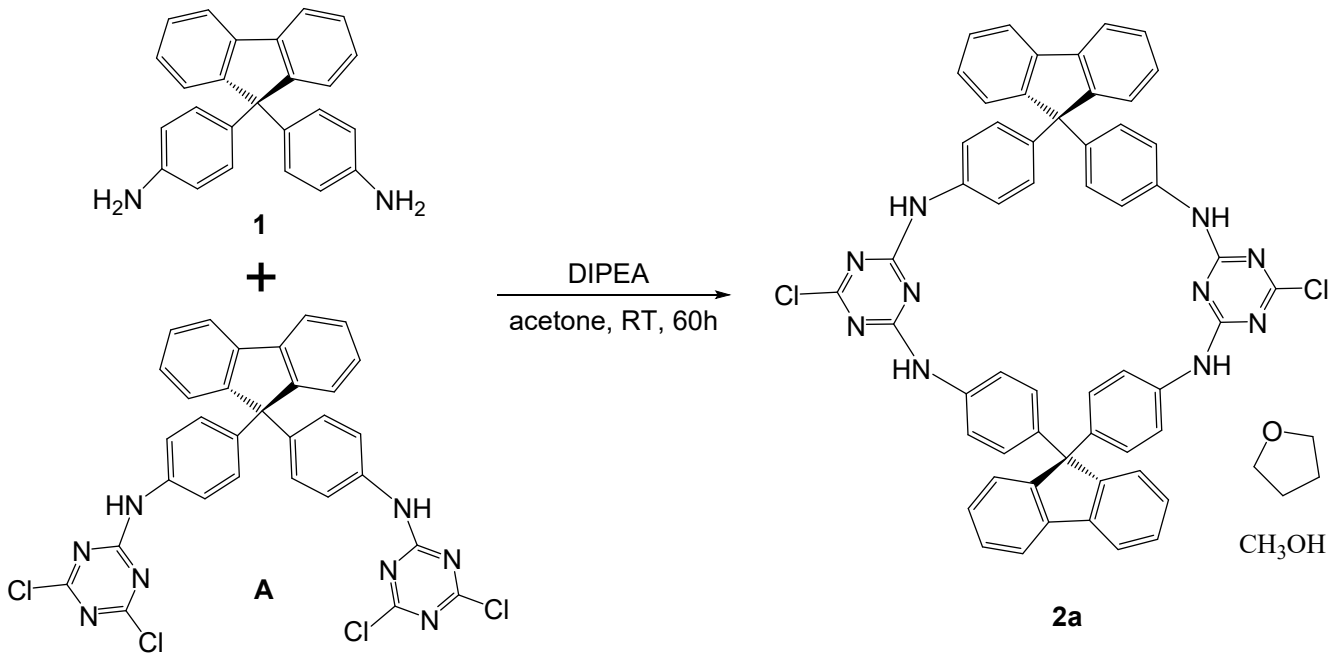
1000
750
500
250
0
402.803
644.431
441.027
366.875
350
400
450
500
550
600
650
700
750
m/z

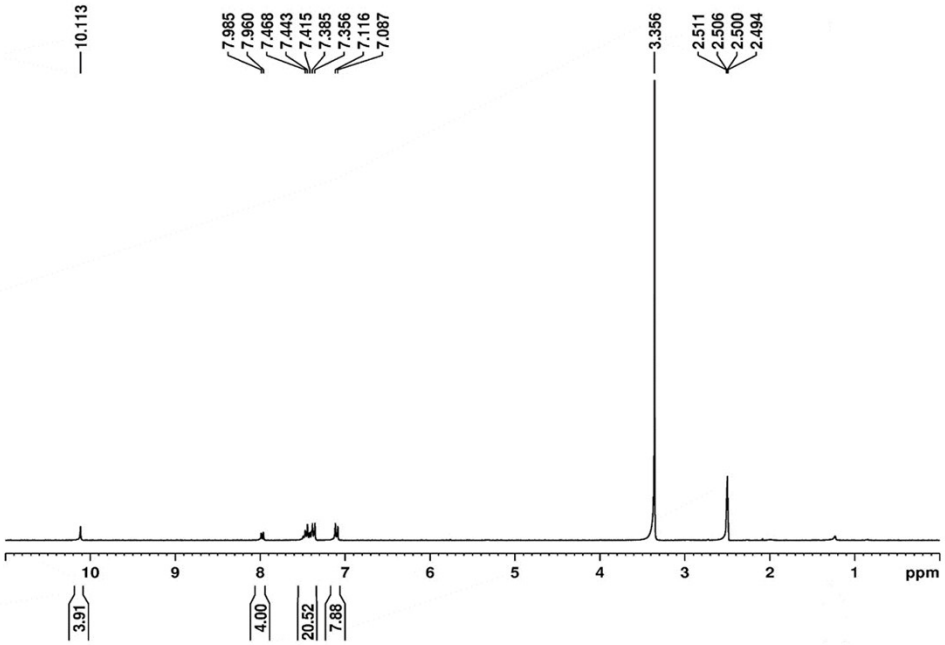
Synthesis of macrocycle 2a



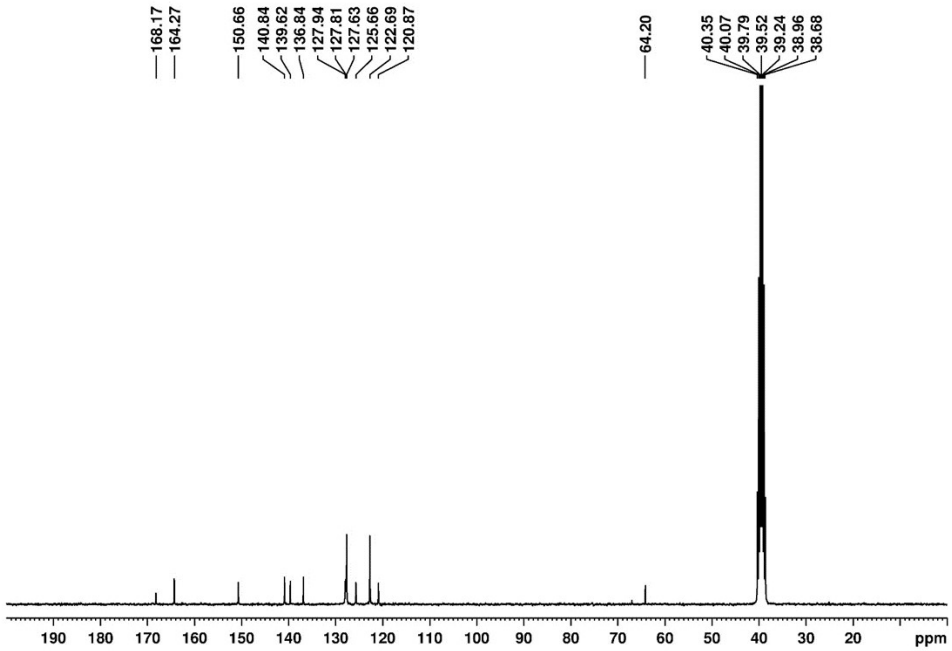
Intermediate **A** (0.644 g, 1.0 mmol) in acetone (90 mL) and 9,9-bis(4-aminophenyl)fluorene **1** (0.348 g, 1.0 mmol) in acetone (90 mL) were simultaneously added to N,N-diisopropylethylamine (0.310 g, 2.4 mmol) in acetone (200 mL) gradually at room temperature and then stirred for 60 h. After the reaction (confirmed by TLC), solvent was removed at reduced pressure to give a solid which was further recrystallized by THF-MeOH (1:2), yielding macrocycle **2a** in 60% (0.60g)

^{1}H NMR (300 MHz, DMSO-D_6, 25 °C, TMS): δ , 7.10 (d, *J*=8.7, 8H, 8×Ar-H), 7.35-7.46 (m, 20H, 20×Ar-H), 7.97 (d, *J*=7.5, 4H, 4×Ar-H), 10.11 (s, 4H, 4×NH) ppm. ^{13}C NMR (75 MHz, DMSO-D_6, 25 °C, TMS): δ 64.20, 120.87, 122.69, 125.66, 127.63, 127.81, 127.94, 136.84, 139.62, 140.84, 150.66, 164.27, 168.17 ppm. HRMS cacld for $C_{56}H_{36}Cl_2N_{10}$ $[M]^+$: 919.2580; found 919.2574. Elemental analysis calcd for $C_{56}H_{36}Cl_2N_{10}$+MeOH: C 71.92; H 4.24; N 14.71 %; found C 71.89; H 4.05; N 14.80 %.

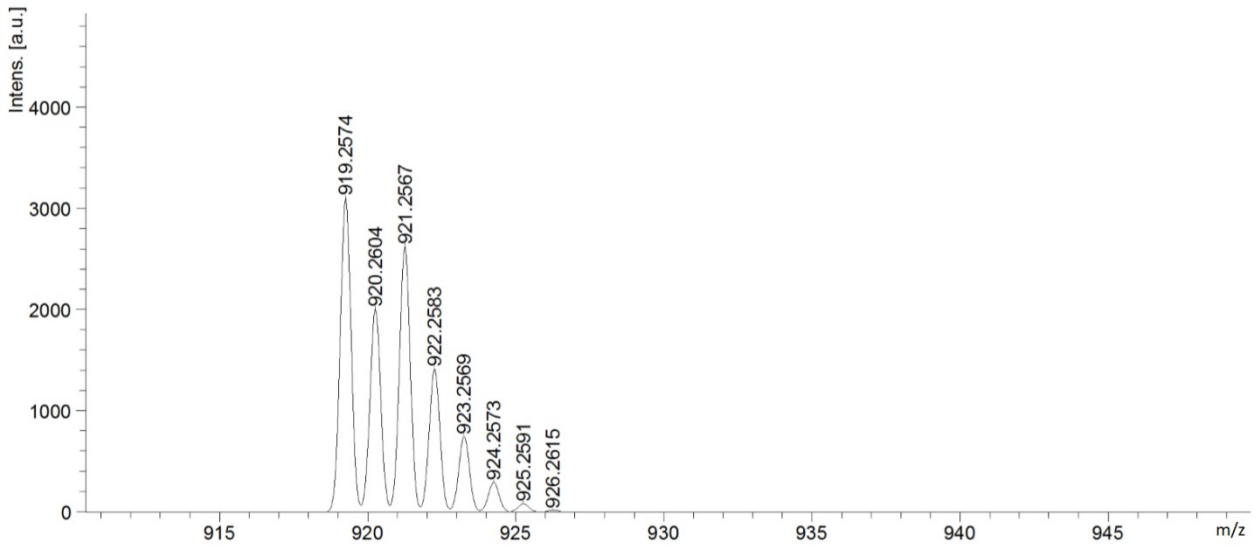
^{1}H NMR of **2a**


10.113
7.985
7.960
7.468
7.443
7.415
7.385
7.356
7.116
7.087
3.356
2.511
2.506
2.500
2.494
10
9
8
7
6
5
4
3
2
1
ppm
3.91
4.00
20.52
7.88

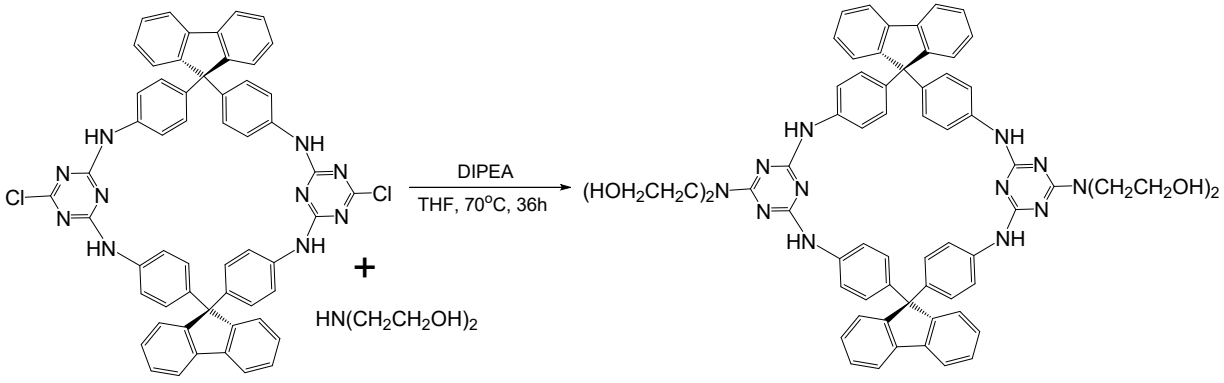
^{13}C NMR of **2a**


168.17
164.27
150.66
140.84
139.62
136.84
127.94
127.81
127.63
125.66
122.69
120.87
64.20
40.35
40.07
39.79
39.52
39.24
38.96
38.68
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

HRMS of 2a


Intens. [a.u.]
4000
3000
2000
1000
0
919.2574
920.2604
921.2567
922.2583
923.2569
924.2573
925.2591
926.2615
915 920 925 930 935 940 945 m/z

Synthesis of macrocycle 2b

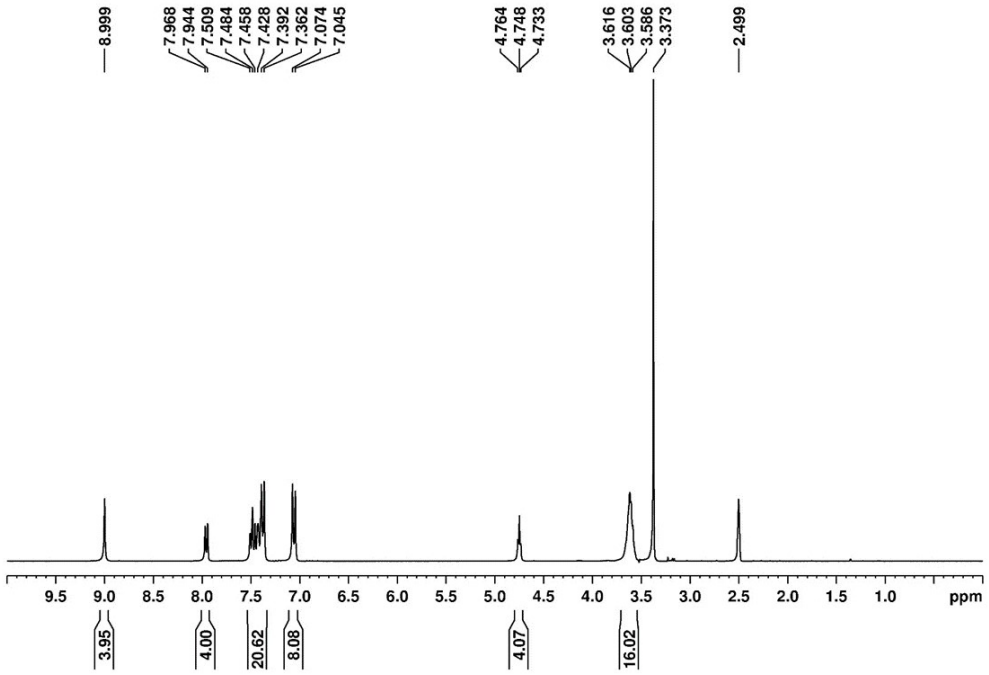


2a **2b**

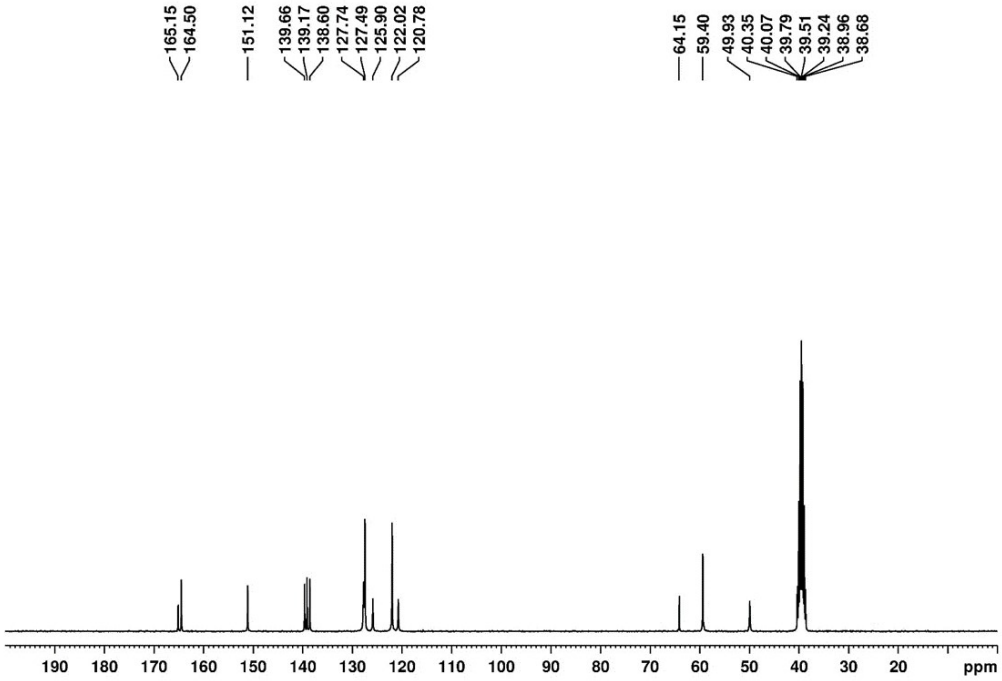
Compound **2a** (0.46 g, 0.5 mmol), diethanolamine (0.52 g, 5.0 mmol) and N,N-diisopropylethylamine (0.15 g, 1.2 mmol) were added to THF (25 mL) and then heated at 70 °C for 36h. After the reaction (confirmed by TLC), solvent was removed at reduced pressure to give a solid which was further purified by chromatography (SiO_2: 20 x 2.2 cm, eluates: THF-hexane [3:1]) and then recrystallized by THF-hexane (2:1), giving macrocycle **2b** in 72% (0.38 g).

^{1}H NMR (300 MHz, DMSO-D_6, 25 °C, TMS): δ 3.57-3.62 (m, 16H, 8×CH_2), 4.74 (t, *J*=4.8, 4H, 4×OH), 7.05 (d, *J*=8.7, 8H, 8×Ar-H), 7.36-7.50 (m, 20H, 20×Ar-H), 7.95 (d, *J*=7.2, 4H, 4×Ar-H), 8.99 (s, 4H, 4×NH) ppm. ^{13}C NMR (75 MHz, DMSO-D_6, 25 °C, TMS): δ 49.93, 59.40, 64.15, 120.78, 122.02, 125.90, 127.49, 127.74, 138.60, 139.66, 151.12, 164.50, 165.15 ppm. HRMS cacld for $C_{64}H_{56}N_{12}O_4$ $[M]^+$: 1057.4626; found 1057.4620. Elemental analysis calcd for $C_{68}H_{64}N_{12}$+H_2O+2THF: C 70.92; H 6.12; N 13.78 %; found C 70.61; H 6.03; N 13.88 %.

^{1}H NMR of **2b**



^{13}C NMR of **2b**


165.15
164.50
151.12
139.66
139.17
138.60
127.74
127.49
125.90
122.02
120.78
64.15
59.40
49.93
40.35
40.07
39.79
39.51
39.24
38.96
38.68
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

HRMS of **2b**

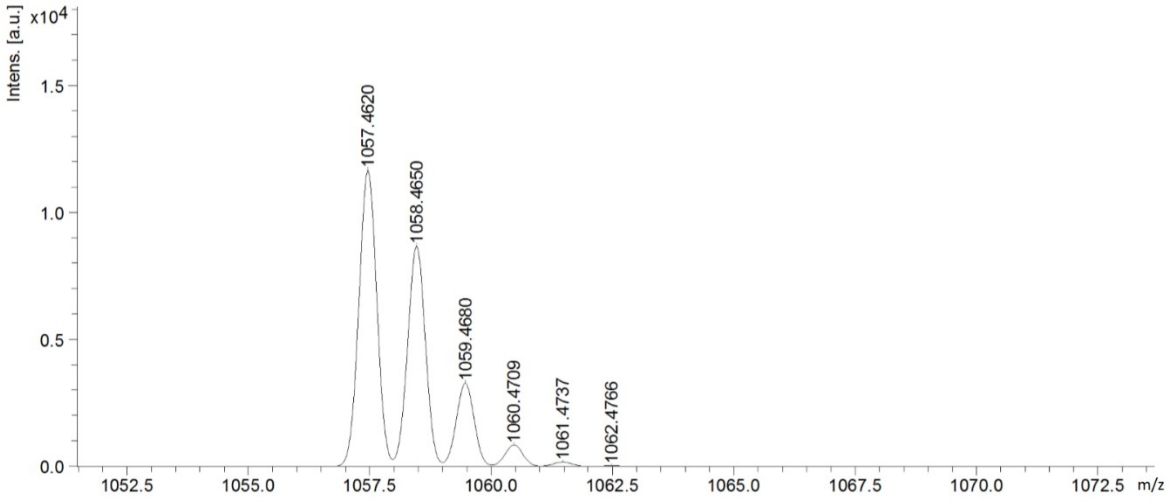
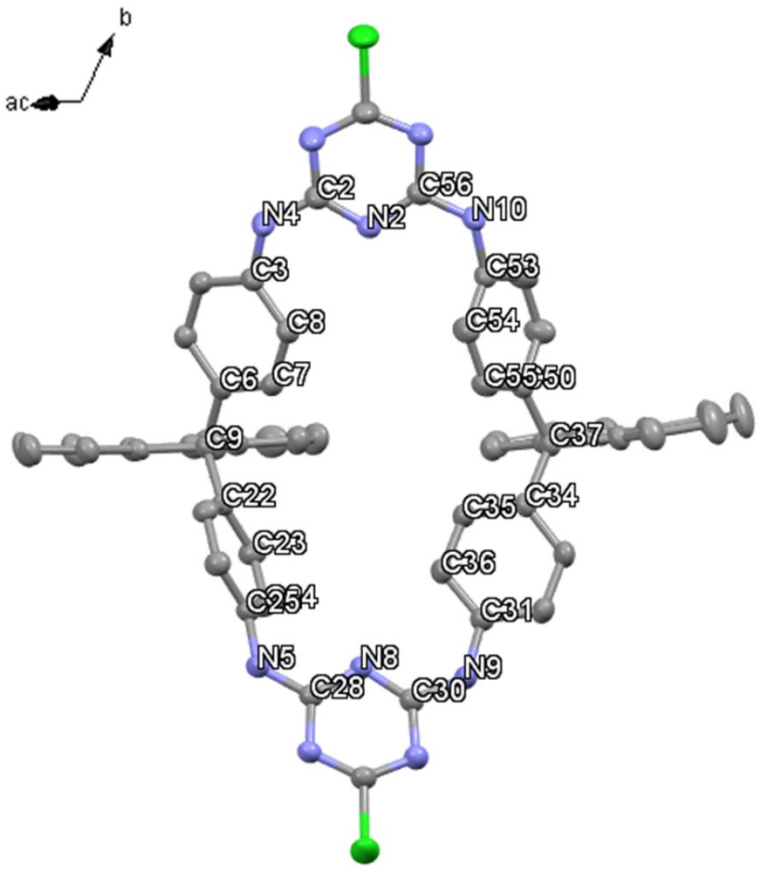

Intens. [a.u.]
x10^4
1.5
1.0
0.5
0.0
1057.4620
1058.4650
1059.4680
1060.4709
1061.4737
1062.4766
1052.5 1055.0 1057.5 1060.0 1062.5 1065.0 1067.5 1070.0 1072.5 m/z

Table S1. Crystal data and structure refinement for **2a•1THF•1MeOH**. (Squeezed THF & CH_3OH, CCDC#2328542)

Identification code	shelx
Empirical formula	C61 H48 Cl2 N10 O2 (C56 H36 Cl2 N10+THF+MeOH)
Formula weight	1024.02
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1

Unit cell dimensions	a = 13.5359(11) Å	α= 102.627(3)°.
	b = 14.6708(11) Å	β= 100.704(3)°.
	c = 16.4233(13) Å	γ = 114.701(3)°.
Volume	2746.4(4) Å^3	
Z	2	
Density (calculated)	1.112 Mg/m^3	
Absorption coefficient	0.162 mm^{-1}	
F(000)	952	
Crystal size	0.270 x 0.100 x 0.050 mm^3	
Theta range for data collection	2.175 to 25.129°.	
Index ranges	-16<=h<=16, -17<=k<=17, -19<=l<=19	
Reflections collected	74086	
Independent reflections	9772 [R(int) = 0.0770]	
Completeness to theta = 25.129°	99.5 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9772 / 0 / 613	
Goodness-of-fit on F^2	1.020	
Final R indices [I>2sigma(I)]	R1 = 0.0423, wR2 = 0.1060	
R indices (all data)	R1 = 0.0563, wR2 = 0.1157	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.318 and -0.354 e.Å^{-3}	

Table S2. Bond lengths [Å] and angles [°] for **2a•1THF•1MeOH** (CCDC#2328542).

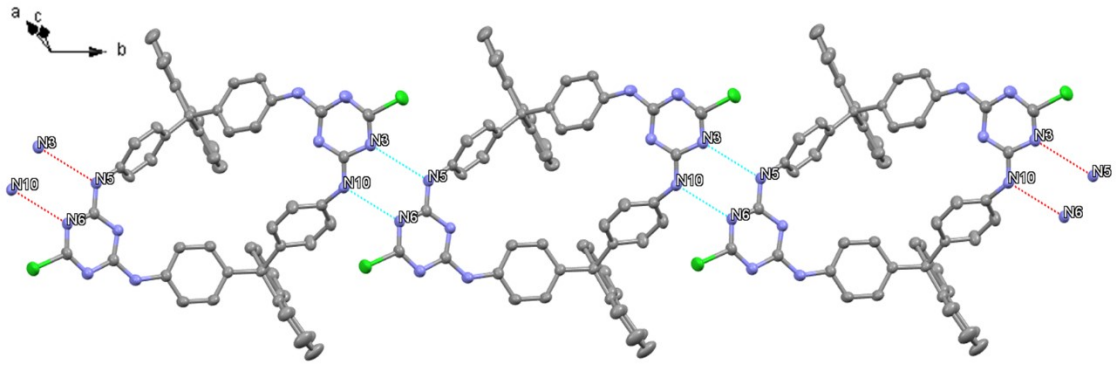


C56	N2	1.339(3)	N2	C2	N4	120.5(2)
N2	C2	1.330(2)	C2	N4	C3	128.3(2)
C2	N4	1.349(3)	N4	C3	C8	124.1(2)
N4	C3	1.413(3)	C3	C8	C7	120.0(2)
C3	C8	1.386(2)	C8	C7	C6	121.8(2)
C8	C7	1.388(3)	C7	C6	C9	121.7(2)
C7	C6	1.390(3)	C6	C9	C22	112.0(2)
C6	C9	1.541(3)	C9	C22	C23	121.8(2)
C9	C22	1.543(2)	C22	C23	C24	121.5(2)
C22	C23	1.385(2)	C23	C24	C25	119.8(2)
C23	C24	1.390(3)	C24	C25	N5	120.5(2)
C24	C25	1.381(3)	C25	N5	C28	124.7(2)
C25	N5	1.435(2)	N5	C28	N8	119.1(2)
N5	C28	1.341(2)	C28	N8	C30	114.4(2)
C28	N8	1.341(3)	N8	C30	N9	120.6(2)
N8	C30	1.327(2)	C30	N9	C31	131.6(2)
C30	N9	1.354(3)	N9	C31	C36	124.6(2)
N9	C31	1.415(3)	C31	C36	C35	119.2(2)

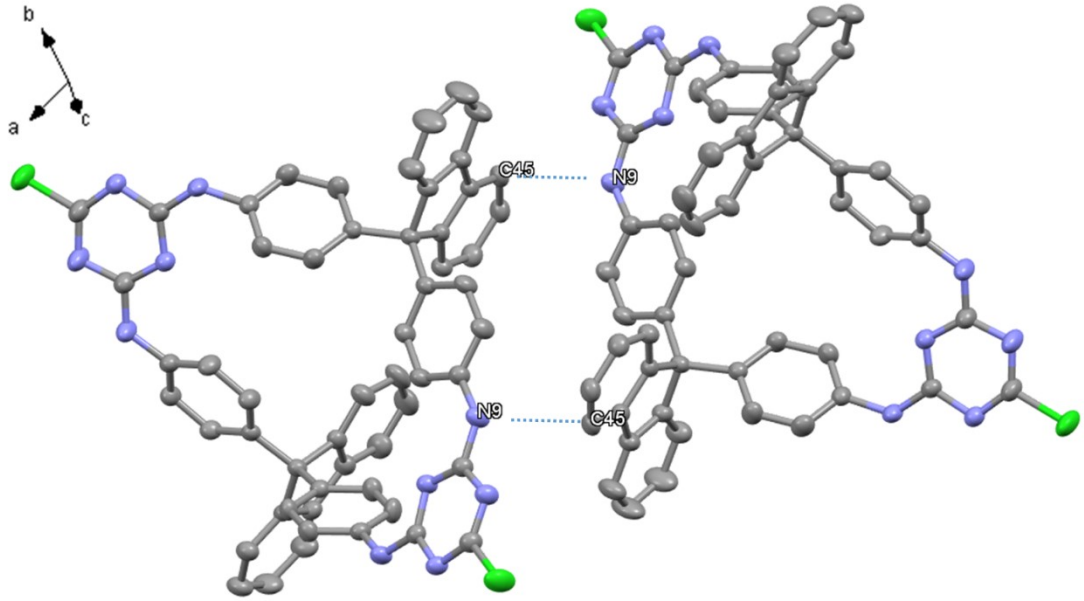
C31	C36	1.394(2)	C36	C35	C34	122.5(2)
C36	C35	1.388(3)	C35	C34	C37	122.6(2)
C35	C34	1.392(3)	C34	C37	C50	116.3(2)
C34	C37	1.535(3)	C37	C50	C55	125.5(2)
C37	C50	1.544(2)	C50	C55	C54	121.3(2)
C50	C55	1.384(3)	C55	C54	C53	120.2(2)
C55	C54	1.397(2)	C54	C53	N10	122.9(2)
C54	C53	1.376(3)	C53	N10	C56	126.7(2)
C53	N10	1.422(2)	N10	C56	N2	119.6(2)
N10	C56	1.334(2)	C56	N2	C2	114.6(2)

Table S3. The intermolecular H-bond (NH-N, NH-C, CH-Cl) and π-π (CH-π, π-π)

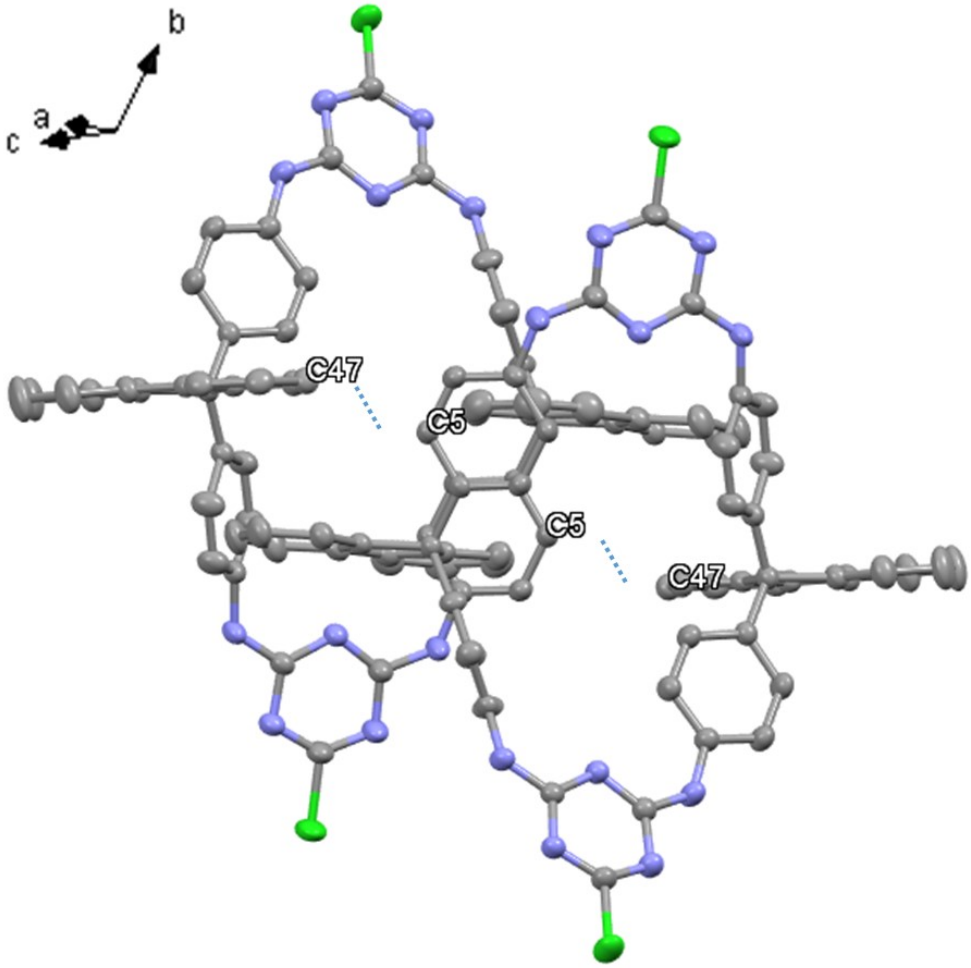
interactions of macrocycle **2a** (THF and MeOH omitted) in the framework.



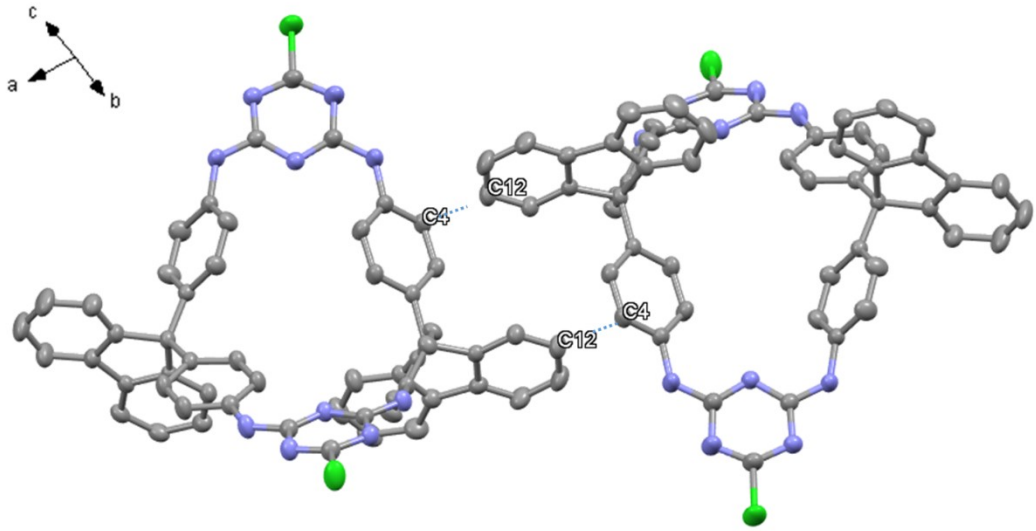
D-H…A	D-H length(Å)	H…A length(Å)	D…A length(Å)	D-H…A angle(°)
N(5)-H(5A)···N(3)	0.8802(20)	2.2409(21)	3.0881(29)	161.464(128)
N(10)-H(10)···N(6)	0.8793(20)	2.0700(19)	2.9200(28)	162.325(123)



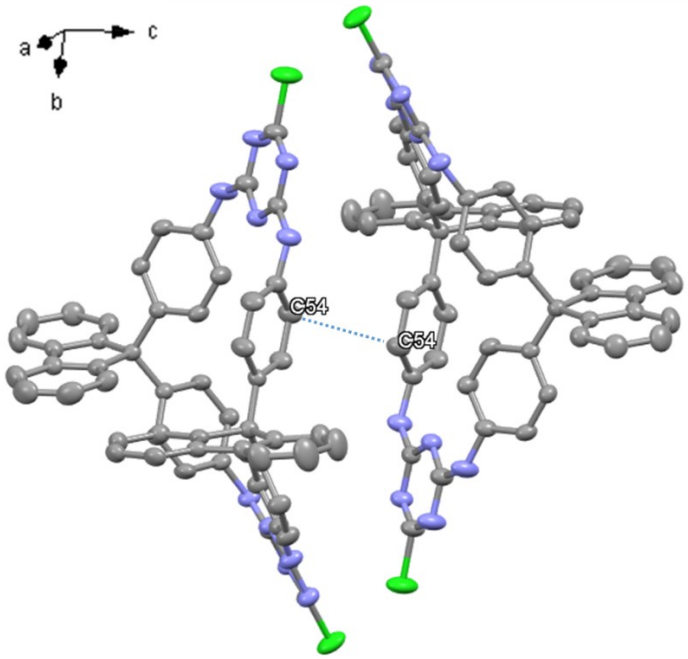
D-H…A	D-H length(Å)	H…A length(Å)	D…A length(Å)	D-H…A angle(°)
N(9)-H(9)···C(45)	0.8799(12)	2.8774(15)	3.7169(19)	160.108(114)
C(45)-H(45)···N(9)	0.9499(23)	3.4887(14)	3.7169(19)	96.423(125)



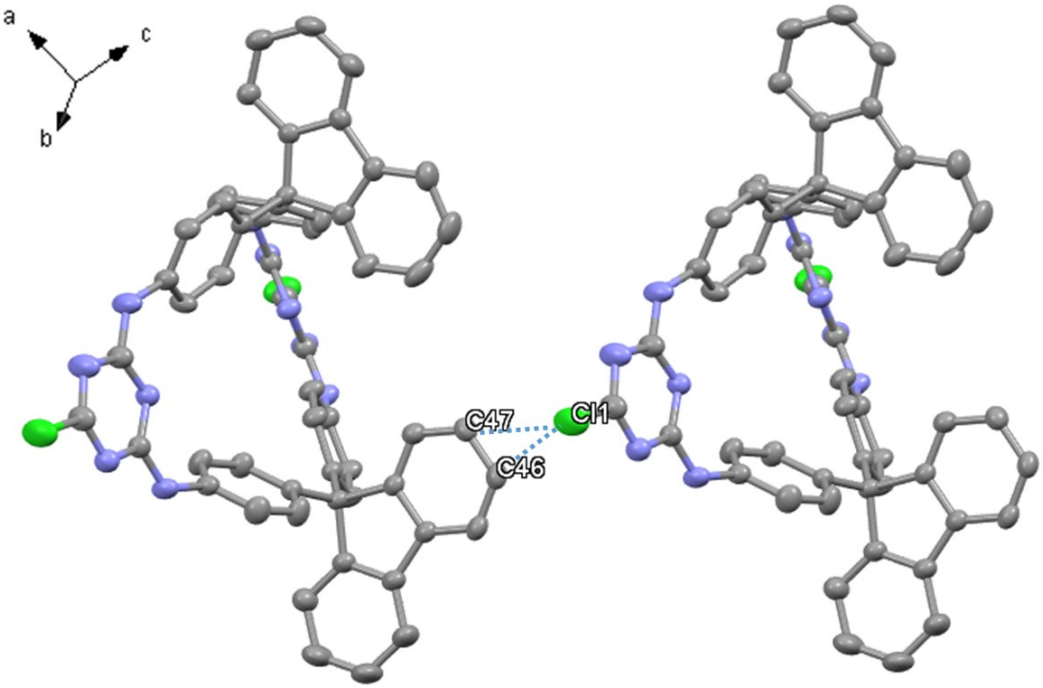
D-H…A	D-H length(Å)	H…A length(Å)	D…A length(Å)	D-H…A angle(°)
C(5)-H(5)⋯C(47)	0.9492(19)	2.9627(20)	3.7529(26)	141.561(108)
C(47)-H(47)⋯C(5)	0.9509(21)	2.9847(18)	3.7529(26)	138.813(115)



D-H…A	D-H length(Å)	H…A length(Å)	D…A length(Å)	D-H…A angle(°)
C(12)-H(12)···C(4)	0.9503(25)	2.7902(24)	3.5392(37)	136.362(167)
C(4)-H(4)···C(12)	0.9504(14)	3.7964(28)	3.5392(37)	67.256(126)



D-H…A	D-H length(Å)	H…A length(Å)	D…A length(Å)	D-H…A angle(°)
C(54)-H(54)···C(54)	0.9505(24)	3.0865(19)	3.3202(30)	95.806(128)



D-H…A	D-H length(Å)	H…A length(Å)	D…A length(Å)	D-H…A angle(°)
C(46)-H(46)···Cl(1)	0.9507(24)	3.1891(7)	3.2693(23)	86.356(130)
C(47)-H(47)···Cl(1)	0.9509(21)	3.2946(5)	3.3403(19)	84.494(127)

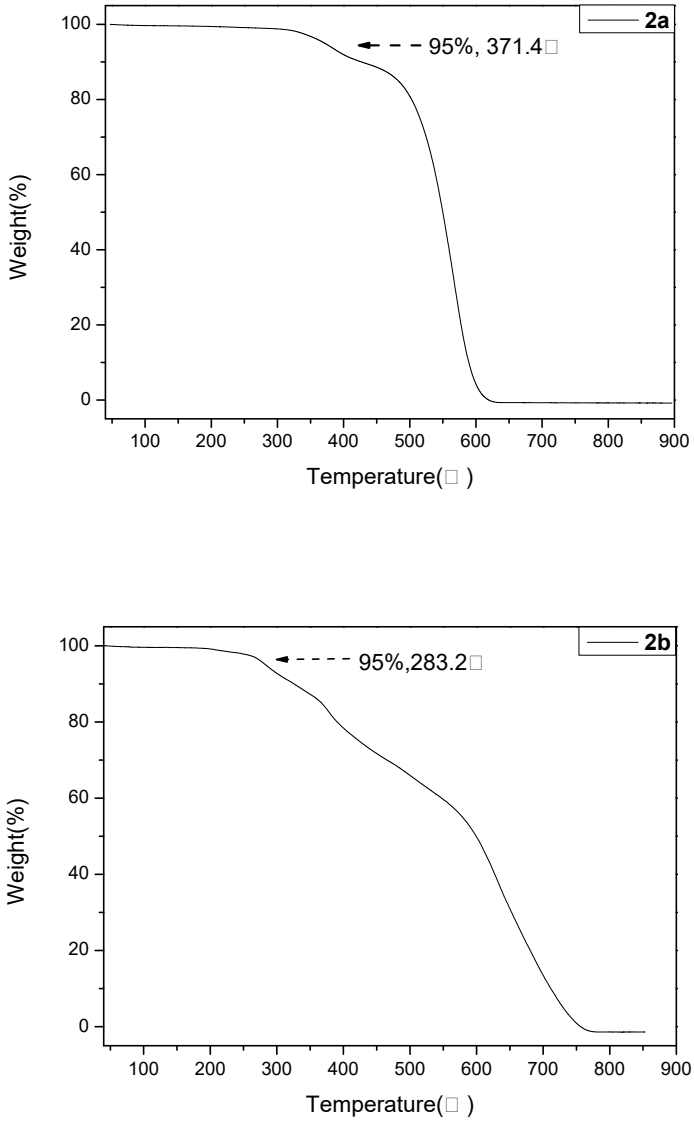


Figure S1. Thermogravimetric analysis of dried **2a** and **2b** from 50 to 850 °C at a heating rate of 10 °C min^{-1} under an N_2 atmosphere.

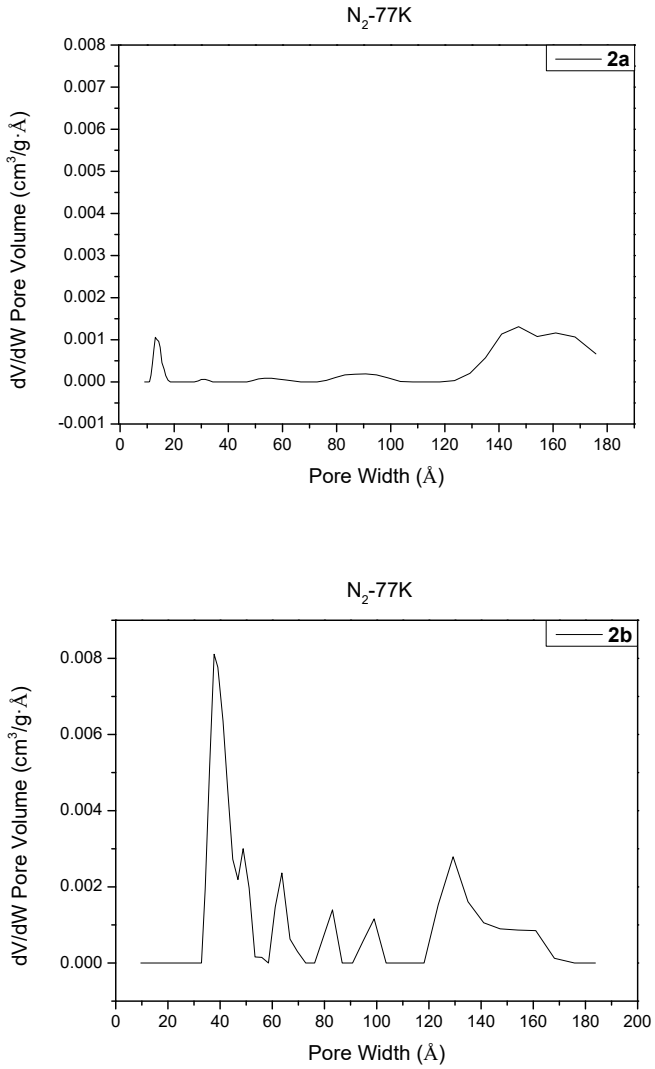


Figure S2. The pore size distributions of **2a** and **2b**, calculated by NLDFT based on their N_2 isotherms at 77 K.

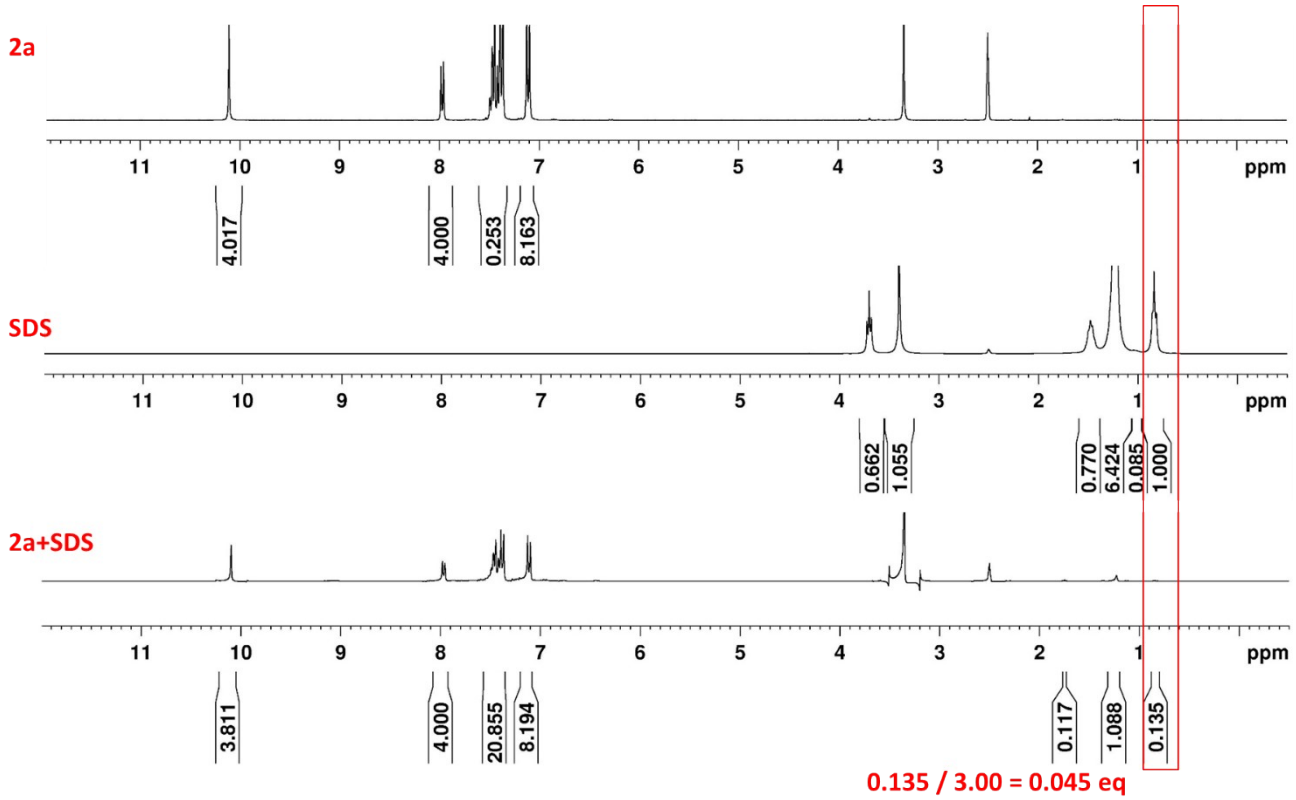
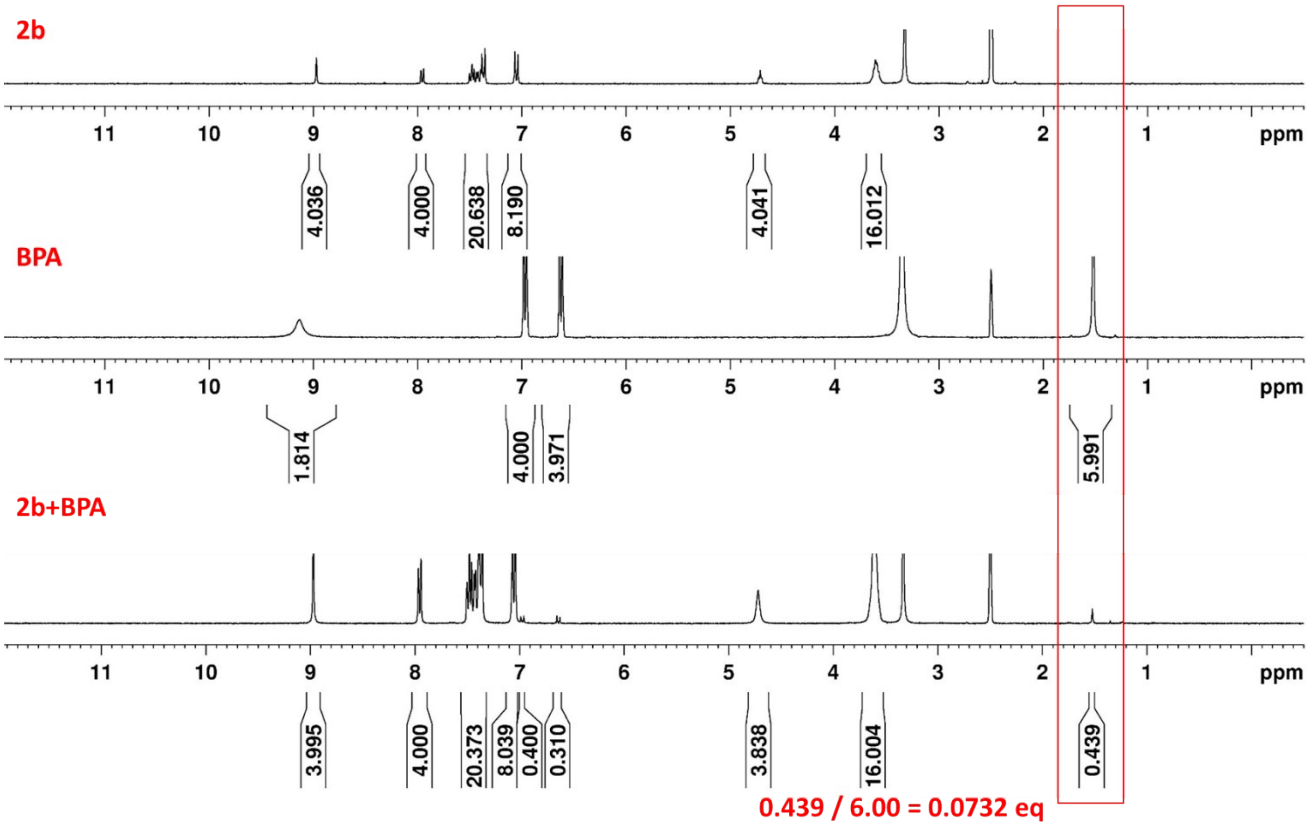
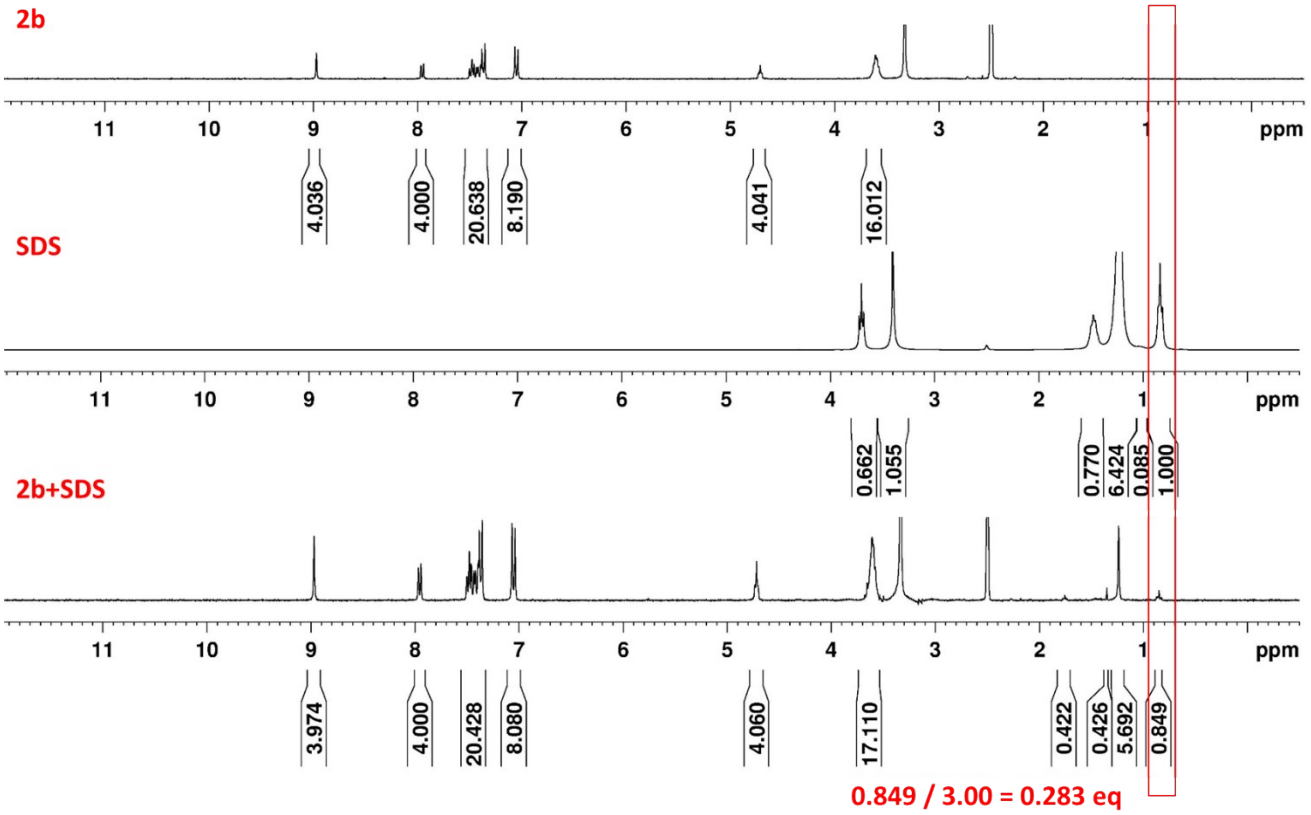


Figure S3. The 1H-NMR spectra of **2a**, SDS and **2a**-SDS in showing the adsorption of SDS by **2a**.


2b
4.036
4.000
20.638
8.190
4.041
16.012
BPA
1.814
4.000
3.971
5.991
2b+BPA
3.995
4.000
20.373
8.039
0.400
0.310
3.838
16.004
0.439
0.439 / 6.00 = 0.0732 eq


2b
4.036
4.000
20.638
8.190
4.041
16.012
SDS
0.662
1.055
0.770
6.424
0.085
1.000
2b+SDS
3.974
4.000
20.428
8.080
4.060
17.110
0.422
0.426
5.692
0.849
0.849 / 3.00 = 0.283 eq

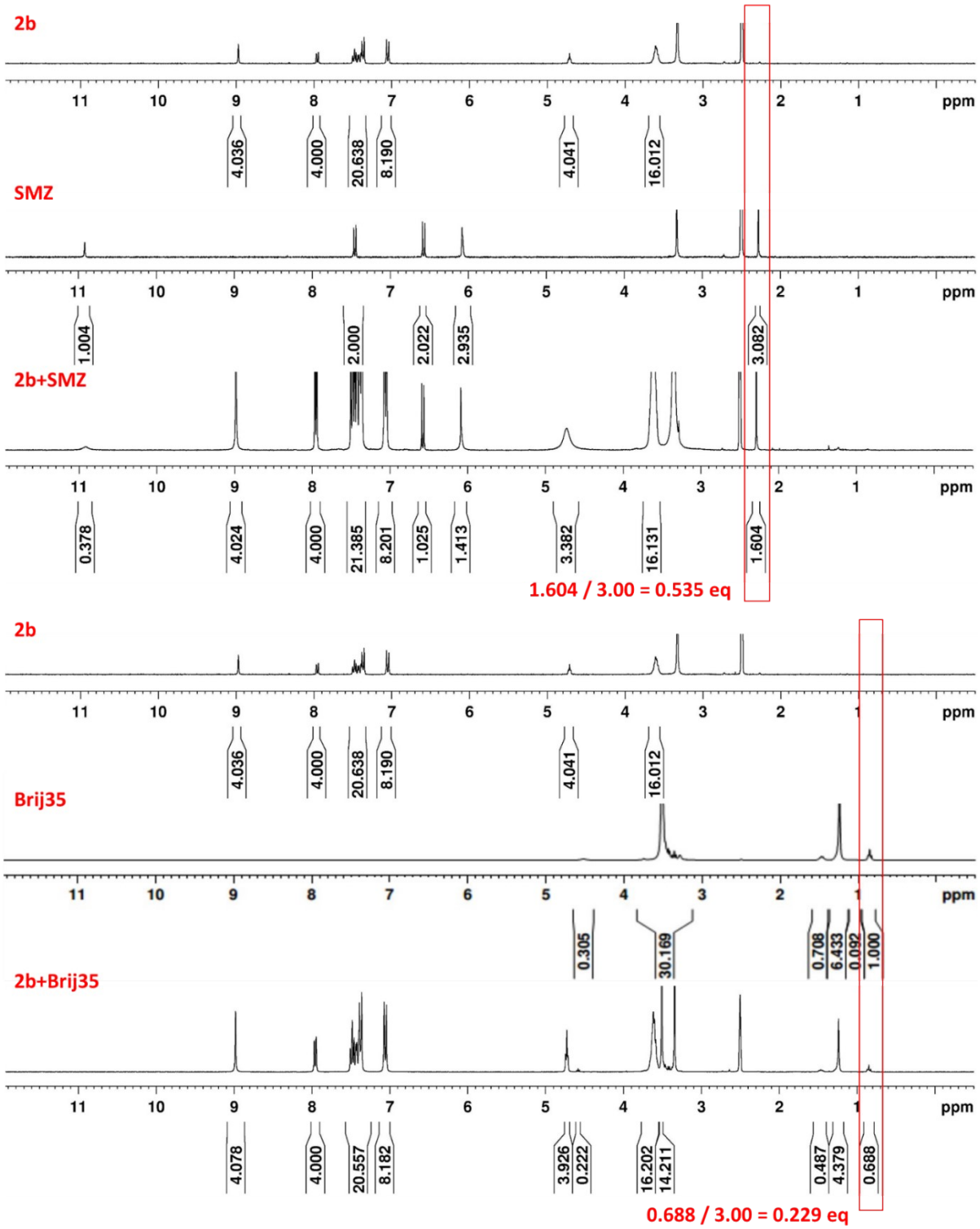
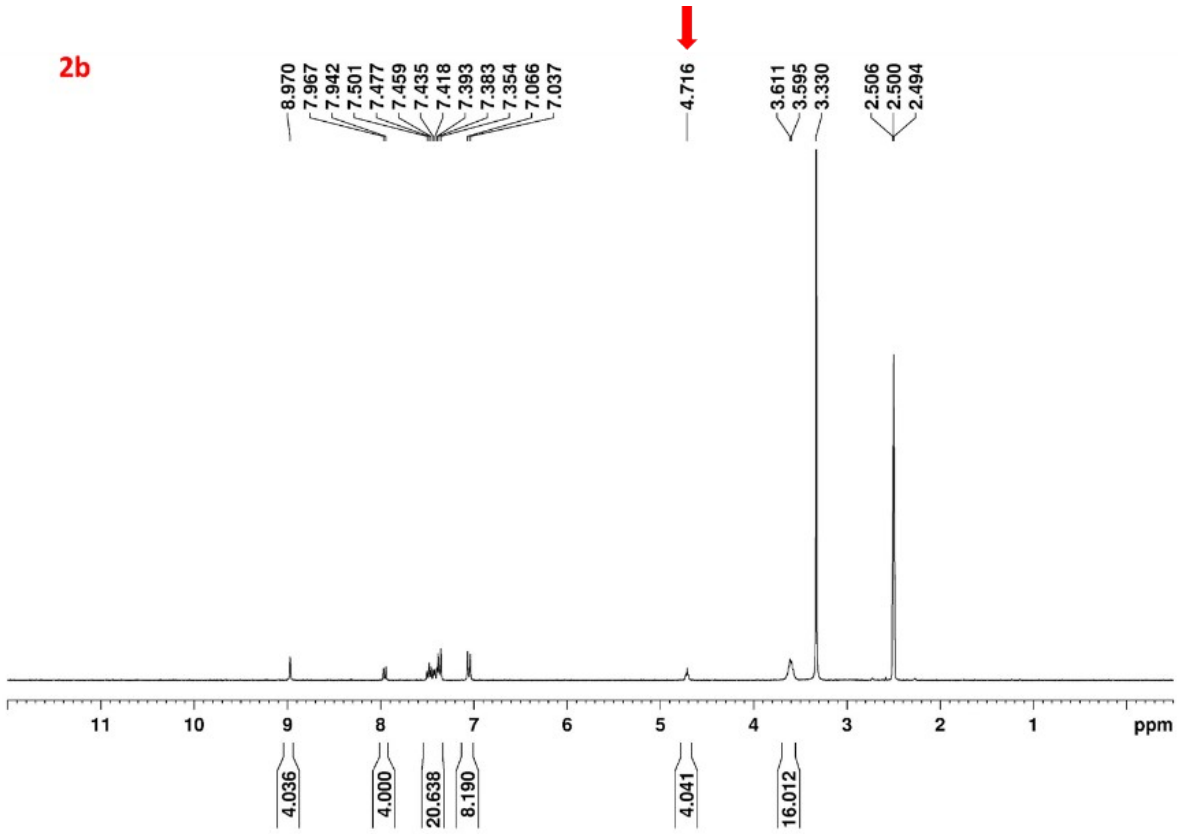
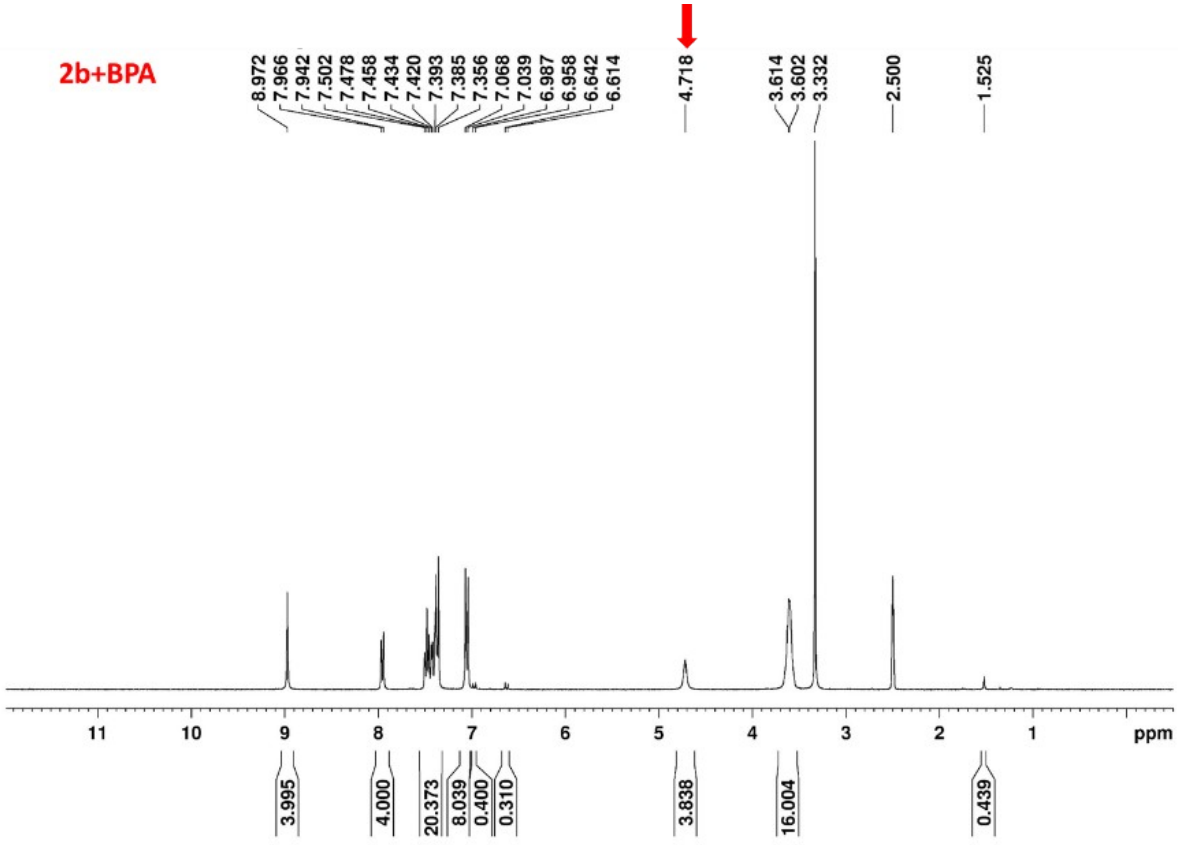
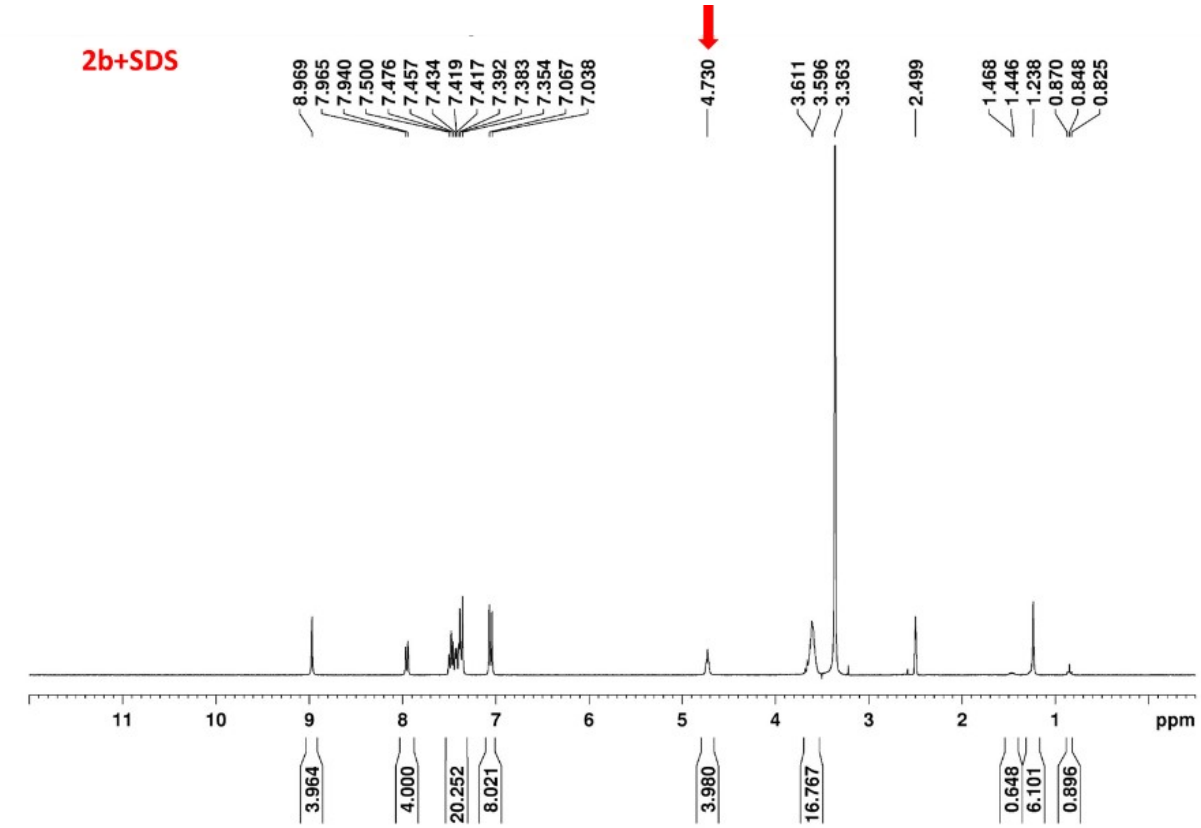
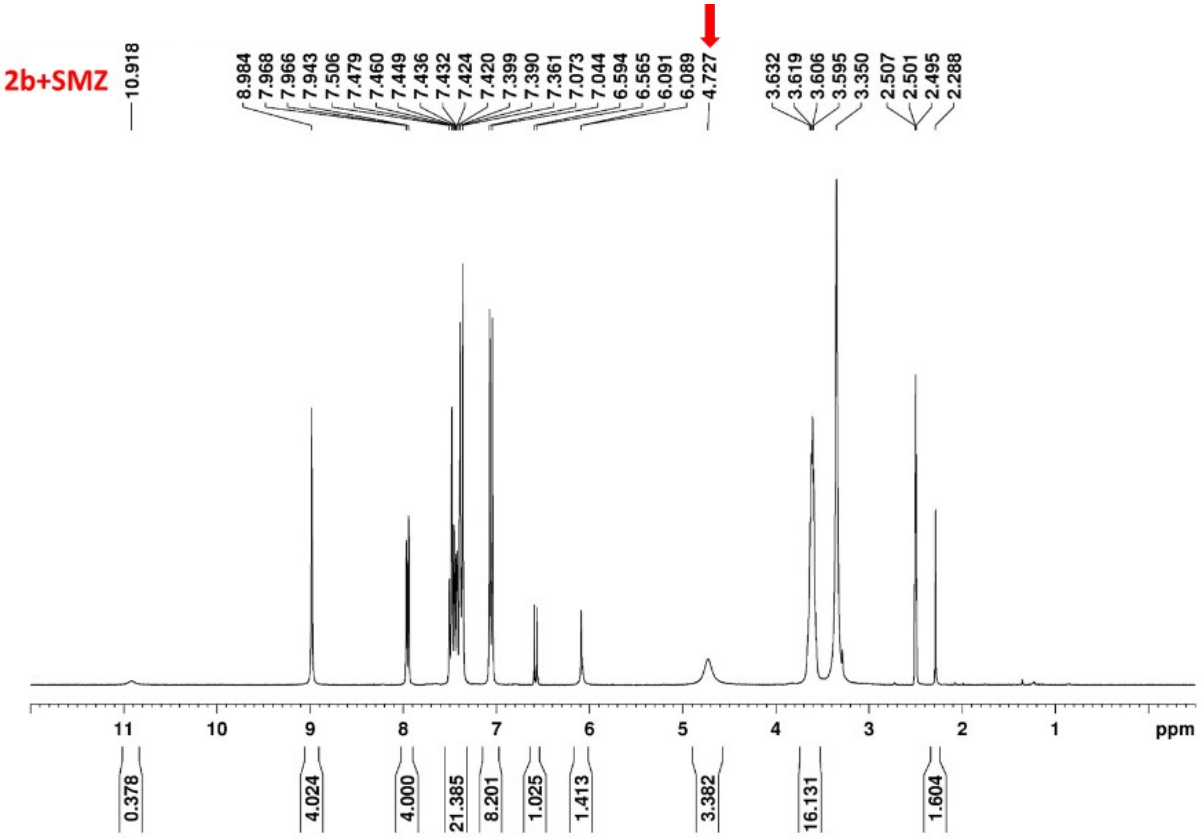


Figure S4. The 1H-NMR spectra of **2b** with BPA, SDS, SMZ and Brij35, respectively, in showing their adsorption by **2b**.


2b
8.970
7.967
7.942
7.501
7.477
7.459
7.435
7.418
7.393
7.383
7.354
7.066
7.037
4.716
3.611
3.595
3.330
2.506
2.500
2.494
11
10
9
8
7
6
5
4
3
2
1
ppm
4.036
4.000
20.638
8.190
4.041
16.012


2b+BPA
8.972
7.966
7.942
7.502
7.478
7.458
7.434
7.420
7.393
7.385
7.356
7.068
7.039
6.987
6.958
6.642
6.614
4.718
3.614
3.602
3.332
2.500
1.525
11
10
9
8
7
6
5
4
3
2
1
ppm
3.995
4.000
20.373
8.039
0.400
0.310
3.838
16.004
0.439


2b+SDS
8.969
7.965
7.940
7.500
7.476
7.457
7.434
7.419
7.417
7.392
7.383
7.354
7.067
7.038
4.730
3.611
3.596
3.363
2.499
1.468
1.446
1.238
0.870
0.848
0.825
11
10
9
8
7
6
5
4
3
2
1
ppm
3.964
4.000
20.252
8.021
3.980
16.767
0.648
6.101
0.896


2b+SMZ
10.918
8.984
7.968
7.966
7.943
7.506
7.479
7.460
7.449
7.436
7.432
7.424
7.420
7.399
7.390
7.361
7.073
7.044
6.594
6.565
6.091
6.089
4.727
3.632
3.619
3.606
3.595
3.350
2.507
2.501
2.495
2.288
11
10
9
8
7
6
5
4
3
2
1
ppm
0.378
4.024
4.000
21.385
8.201
1.025
1.413
3.382
16.131
1.604

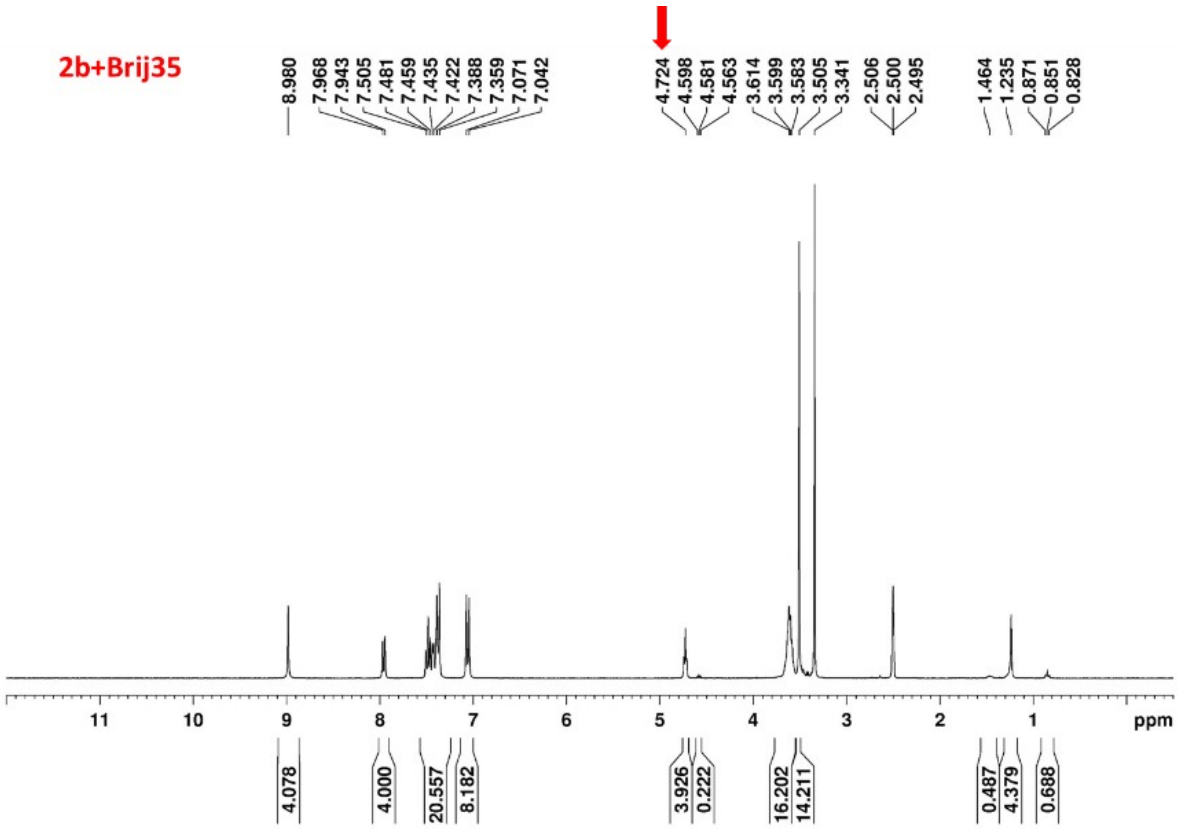


Figure S5. The H-chemical shifts of **2b** and **2b** with BPA, SDS, SMZ and Brij35, respectively.

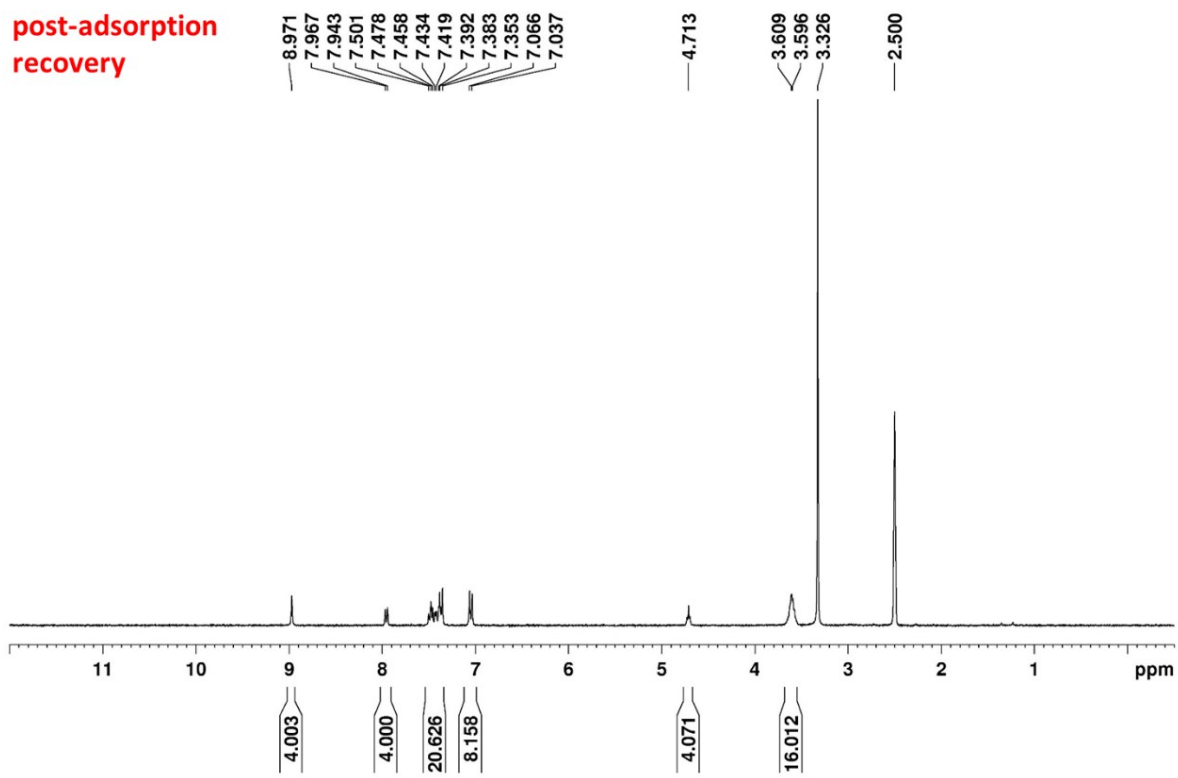


Figure S6. The H-chemical shifts of **2b** after recovery.

1. G. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112-122.