

— *Electronic Supplementary Information* —

A Two-dimensional Hydrogen Bonded Organic Framework Self-assembled from a Three-fold Symmetric Carbamate

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Material and Method

All starting materials were obtained commercially and used as received. Analytical TLC was performed on silica G TLC plate w/UV254 (Sorbent Technologies). ^1H NMR and ^{13}C NMR data were collected on a Bruker Advance 500 spectrometer, and processed with its self-bond software. The chemical shifts in spectra were measured in parts per million (ppm) on the delta (δ) scale relative to the resonance of the solvent peak (CDCl_3 signal as reference, $^1\text{H} = 7.27$ ppm, $^{13}\text{C} = 77.0$ ppm). Electrospray Ionization Mass Spectra (ESI-MS) were obtained using 10 mM ammonium acetate as the matrix on a Time-of-Flight MS G1969A Series 6200 spectrometer (Agilent Technologies Co. Ltd.) with Fragmentor 250V and ESI 5000V. The X-ray data were collected by a Bruker D8 single crystal X-ray diffractometer (Apex II). IR spectra were acquired on a Perkin Elmer Spectrum 400 FT-IR/FT-FIR spectrometer. Melting points of compounds were detected by Melting Point Apparatus SMP10 (Bibby Scientific Ltd., UK) without correction. X-ray powder diffraction spectra were recorded on a X'PERT-PRO X-ray diffractometer (PANalytical, Netherlands) equipped with a 3 KW copper tube X-ray generator of $\lambda = 0.1541\text{nm}$ under 40 mA and 45 KV. Spectra were collected at room temperature in a 2θ range of $3^\circ\sim 35^\circ$ at a scanning rate of $3^\circ/\text{min}$.

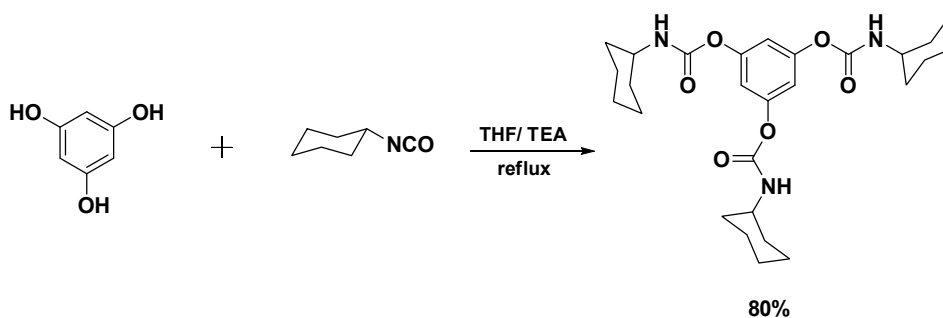
TEM

TEM measurements were performed at Hitachi 7500 TEM with accelerate voltage 80 Kv. A certain amount of compound was weighted precisely in a 20 mL vial, then was dissolved in a solvent using ultrasonic for about 10 min and was heated close to the boiling temperature of the solvent to obtain a homogenous solution. Next, the solution was slowly cooled down in air to room temperature to form self-assemblies and aging overnight. A 100 μL of the above self-assemblies solution was quickly injected into 10 mL water in a 20 mL of vial with vigorous stirring, and then the solution was agitated using ultrasonic for about 10 min and aging overnight. The sample was then dropped to a 200 mesh copper grid with formvar carbon as a support film, and completely dried in air prior to be observed by TEM.

Synthesis of benzene-1, 3, 5-triyl tris(cyclohexylcarbamate) **1**

The building block of the nanosheet benzene-1, 3, 5-triyl tris(cyclohexylcarbamate) **1** was readily synthesized by the reaction of 1,3,5-trihydroxybenzene with isocyanatocyclohexane in a nucleophilic addition in the presence of triethylamine (TEA).

A dried 50 mL round bottom flask equipped with a magnetic stir bar was charged with isocyanatocyclohexane (0.76 g, 6.3 mmol) and a catalytic amount of TEA (4-6 drops) in 5 mL of THF. The mixture was stirred at room temperature for 5 minutes. Phloroglucinol (0.25 g, 2 mmol) in 5 mL of THF was added dropwise within 5 minutes. Then the mixture was refluxed for 22 hours. The mixture was concentrated by evaporating the solvent with a rotavapor and precipitated in 250 mL of ice cold water. The solid product was filtered. The title compound **1** (m.p. 210-212 °C) was obtained as a white solid (0.80 g, 80%) by filtration. ^1H NMR (DMSO- d_6 , δ , ppm): 1.11(m, 3H), 1.20-1.24 (m, 15H), 1.53-1.56 (m, 3H), 1.67-1.70 (m, 6H), 1.80-1.82 (m, 6H), 3.28 (m, 3H), 6.71 (s, 3H), 7.77 (s, 3H); ^{13}C NMR(DMSO- d_6 , δ , ppm): 24.9, 25.4, 32.8, 50.2, 112.1, 151.8, 153.1; IR (Nujol, ν , cm^{-1}) 3325, 3288, 2924, 1712, 1527, 1459, 1143, 1031; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{40}\text{N}_3\text{O}_6$ ($\text{M}+\text{H}^+$) 502.2917, found 502.2911, ($\text{M}+\text{NH}_4^+$) calcd 519.3182, found 519.3177.



Scheme S1. Synthesis of benzene-1, 3, 5-triyl tris(cyclohexylcarbamate) **1**.

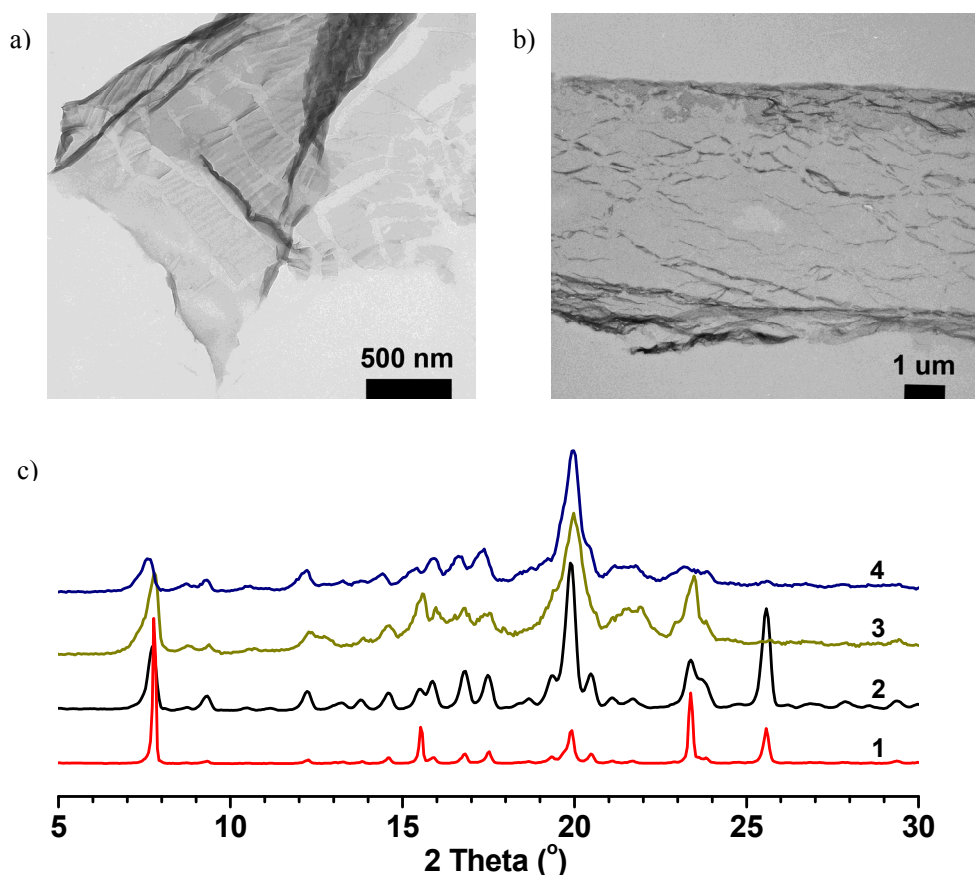


Fig. S1. TEM images of the sheet obtained by injecting 100 μL of (a) 2×10^{-3} M CH₃CN or (b) 2×10^{-3} M THF solution of tri-carbamate **1** into 10 mL of H₂O with stirring and then evaporating the mixed solvent; c) corresponding powder XRD patterns showing the sheets have the same or very similar crystalline isoform as the guest-free crystal **1**: (1) ground single crystals **1** grown in CH₃CN solution; (2) powder **1** obtained directly from the synthesis without further processing; (3) powder of the sheet in (a) obtained by injecting 2×10^{-3} M CH₃CN solution of **1** into H₂O with stirring, and then evaporating the mixed solvent; g) powder of the sheet in (b) obtained by injecting 10^{-3} M EtOAc solution of **1** into H₂O.

Crystal Data of the Nanosheets with /without Guests

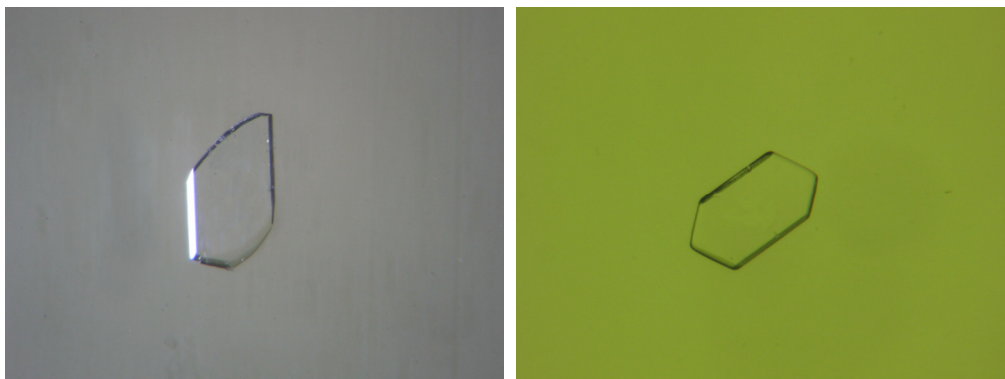


Fig. S2. Crystals of tri-carbamate by slowly evaporating the solvents: (left) **1** obtained from acetonitrile solution; (right) **1**·(THF) obtained from wet THF solution containing 5% water.

Recrystallization and X-ray Structures

In a 20 mL of vial with screw lid, a certain amount of powder of compound **1** was dissolved in a pure solvent or solvent combination to obtain a supersaturated solution by heating. The combined solvent generally consists of a 1:1 ratio of certain solvent and THF. In some cases, a slightly excessive THF may add to obtain a completely clear solution. The solution was then put at ambient temperature to allow the solvent slowly evaporate by gently loosening the lid until single crystals grow.

The X-ray data of the guest-free crystal **1** were collected both at room temperature and 100 K to check thermal response of the sheet structure. The volume of the crystal structure **1**(100K) collected at 100 K decreased 3.3 % and the average hydrogen bond length dropped 0.04 Å compared to the structure **1** at room temperature (See Table S1).

In both **1**·(THF) and **1**, the seven atoms of each carbamate, C_{Ar}-O-(C=O)NHC_R, are near planar. The tri-carbamate molecule contains three stereogenic axes (C_{Ar}-O). Each carbamate group is partially tilted with respect to the core aryl ring to fulfill requirements of the hydrogen bond orientations and close packing of the molecules (See Fig. S3). The torsion angles are -39°, 47°, and 87° in **1**·(THF), -42°, 45°, and -85° in **1**, respectively. The distances of three C_{Ar}-O single bonds connecting the carbamate groups and benzene ring are approximately 1.40 Å. This value is close to a typical bond length of a C-O single bond, which shows only weak conjugation. However, in this supramolecular atropisomer, the hydrogen bonds do not allow the carbamate groups to rotate freely around the C_{Ar}-O axes. Thus, a three dimensional chiral conformation is fixed in the hydrogen bonded network. Since a pair of supramolecular enantiomers appear in each sheet, this hydrogen bonded sheet is racemic while the three reported sister sheets are all chiral.

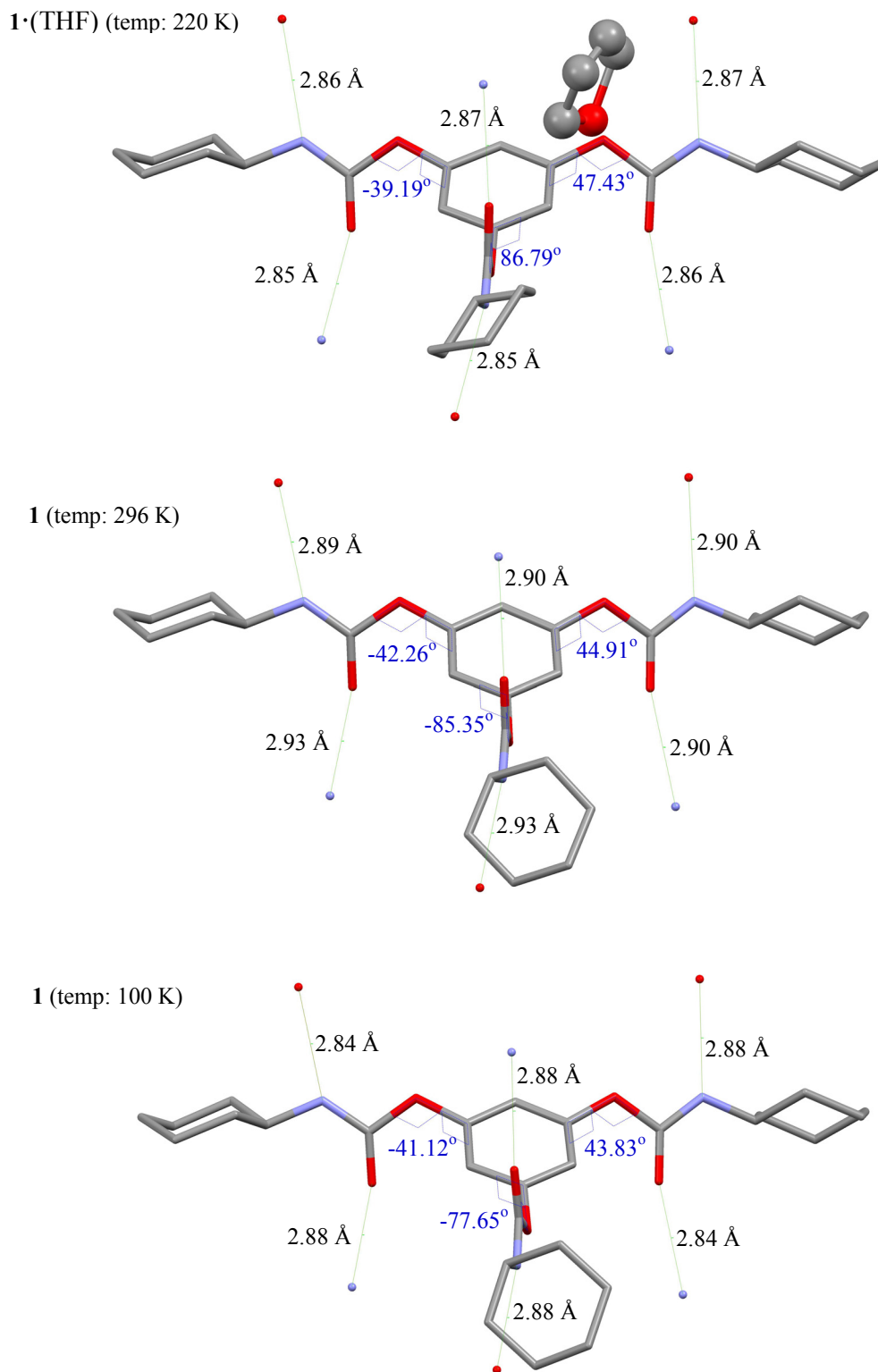


Fig. S3. Hydrogen Bonds and Torsion Angles of **1·(THF)** and **1**.

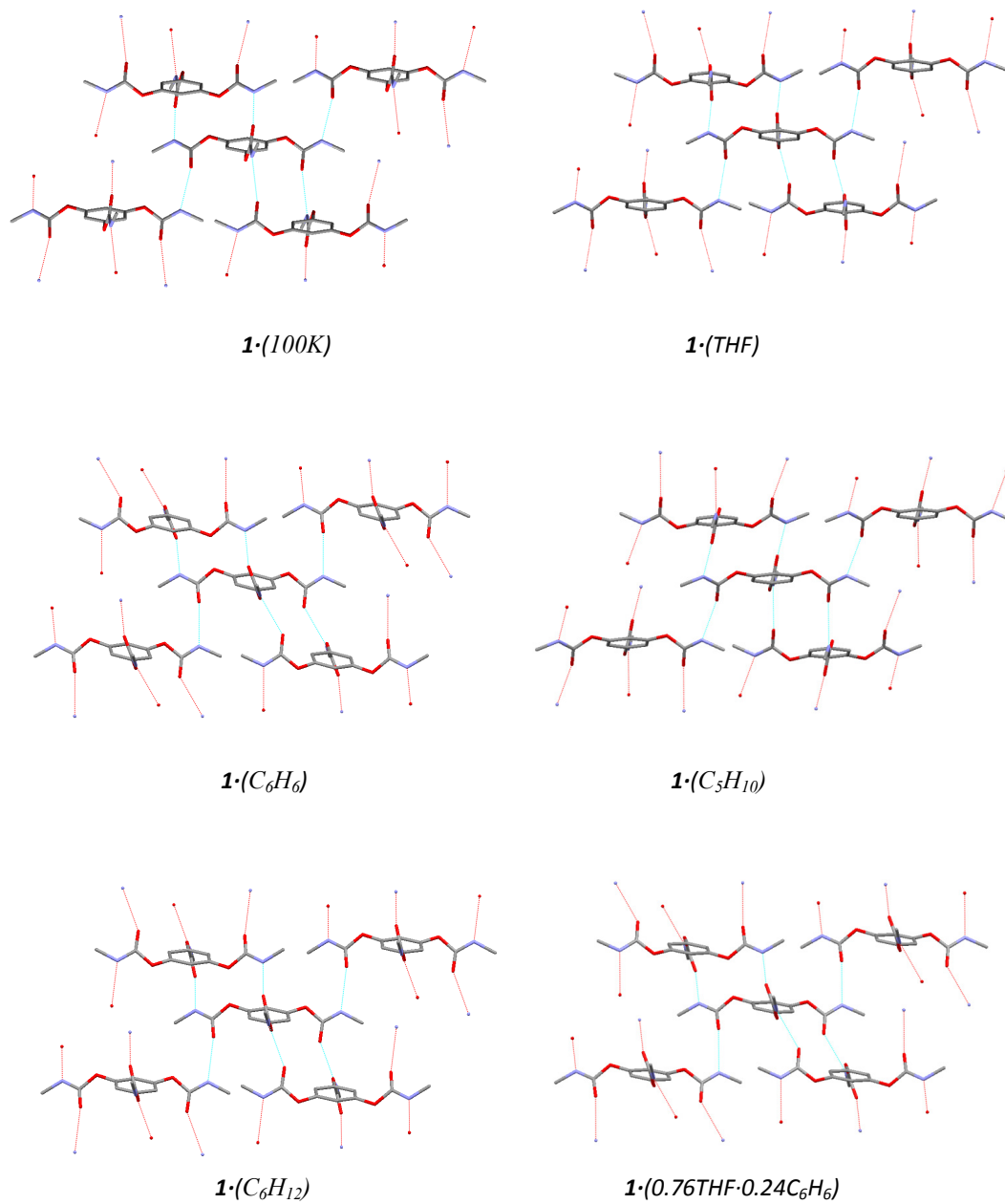


Fig. S4. Hydrogen Bonds Connectivity of **1** and **1**·(Guest).

Table S1. Crystal Data of the Nanosheets with/without Guests.

Crystals	1·(296K)	1·(100K)	1·(THF)	1·(C ₆ H ₆)	1·(C ₅ H ₁₀)	1·(C ₆ H ₁₂)	1·2Guests ^a
CCDC #	941728	941726	941724	941725	941727	941729	961160
Formula	C ₂₇ H ₃₉ N ₃ O ₆	C ₂₇ H ₃₉ N ₃ O ₆	C ₂₇ H ₃₉ N ₃ O ₆ •C ₄ H ₈ O	C ₂₇ H ₃₉ N ₃ O ₆ •C ₆ H ₆	C ₂₇ H ₃₉ N ₃ O ₆ •C ₅ H ₁₀	C ₂₇ H ₃₉ N ₃ O ₆ •C ₆ H ₁₂	C ₂₇ H ₃₉ N ₃ O ₆ •0.76C ₄ H ₈ O 0.24C ₆ H ₆
FW	501.61	501.61	573.72	579.72	571.71	585.77	576.06
Cryst. Size [mm]	.52, .41, .10	.35, .21, .09	.44, .39, .27	.50, .30, .20	.45, .20, .15	.35, .21, .09	.24, .12, .05
Space Group, Z	P-1, 2	P-1, 2	P-1, 2	P-1, 2	P-1, 2	P-1, 2	P-1, 2
a (Å)	9.8219(3)	9.7843(5)	9.6082(7)	8.9512(4)	10.0767(5)	9.3142(5)	9.0114(3)
b (Å)	12.3012(4)	12.0137(6)	12.7842(9)	13.4411(6)	12.0867(5)	12.9790(10)	13.5216(5)
c (Å)	12.6085(4)	12.5621(6)	14.6055(10)	14.6433(6)	14.5514(3)	14.8266(10)	14.3876(5)
α (°)	109.671(2)	109.821(2)	74.979(3)	75.921(2)	72.469(3)	78.059(4)	75.211(2)
β (°)	102.008(2)	102.469(2)	71.027(3)	73.652(2)	70.442(3)	73.016(4)	72.344(2)
γ (°)	94.201(2)	93.990(2)	77.567(3)	71.945(2)	80.967(3)	74.112(2)	72.914(2)
V (Å ³)	1386.00(8)	1339.88(12)	1621.7(2)	1583.64(12)	1589.34(12)	1632.9(2)	1570.0(1)
Temp. (K)	297	100	220	100	150	100	100
ρ _{calc} [g/cm ³]	1.202	1.243	1.175	1.216	1.195	1.191	1.219
μ [mm ⁻¹]	0.085	0.088	0.083	0.084	0.082	0.081	0.084
Radiation Type	Mo	Mo	Mo	Mo	Mo	Mo	Cu
F(000)	540	540	620	624	474	636	622
No of measured refl.	40747	18174	61262	19900	16646	19262	13886
No of independent refl.	6611	4746	7776	9058	6790	9139	5106
No of refl. (I ≥ 2σ)	4848	4000	5832	7693	4527	7188	4040
R1/wR2 (I ≥ 2σ) [%]	7.71/23.39	3.61/8.80	7.60/23.35	4.37/11.55	5.98/16.09	7.62/17.01	4.80/12.35
R1/wR2 (all data) [%]	9.66/25.48	4.44/9.33	9.39/25.60	5.33/12.70	9.13/18.68	9.48/18.37	6.24/13.44
Average H bond length	2.91	2.87	2.86	2.85	2.88	2.86	2.85

a) Although the X-ray data indicated that THF/C₆H₆ ratio 0.6:0.4 was the best fit, multiple NMR experiments showed that THF ratio was about 76%: 0.76=(74.4%+76.7%+78.3%)/3, which was an average of three experiments. We believe the NMR data was more reliable.

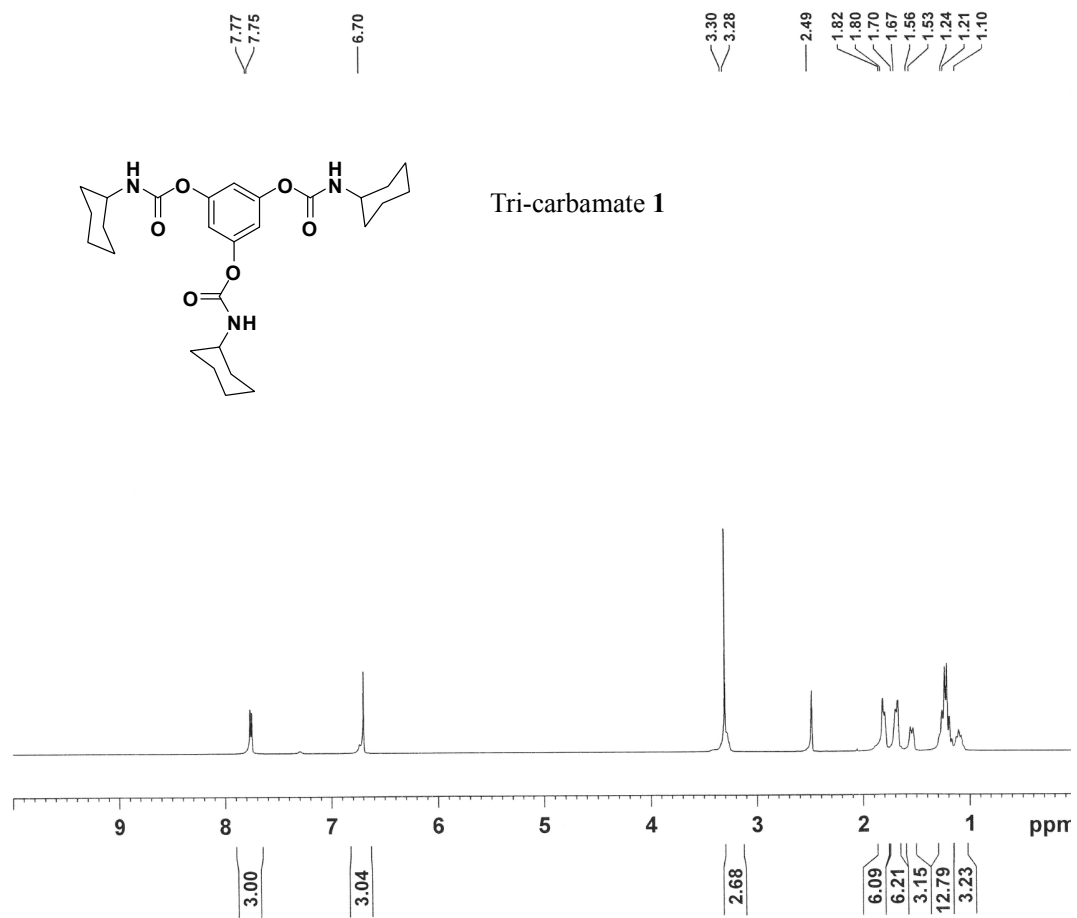


Fig. S5. ^1H NMR spectrum of benzene-1,3,5-triyl tris(cyclohexylcarbamate) **1**.

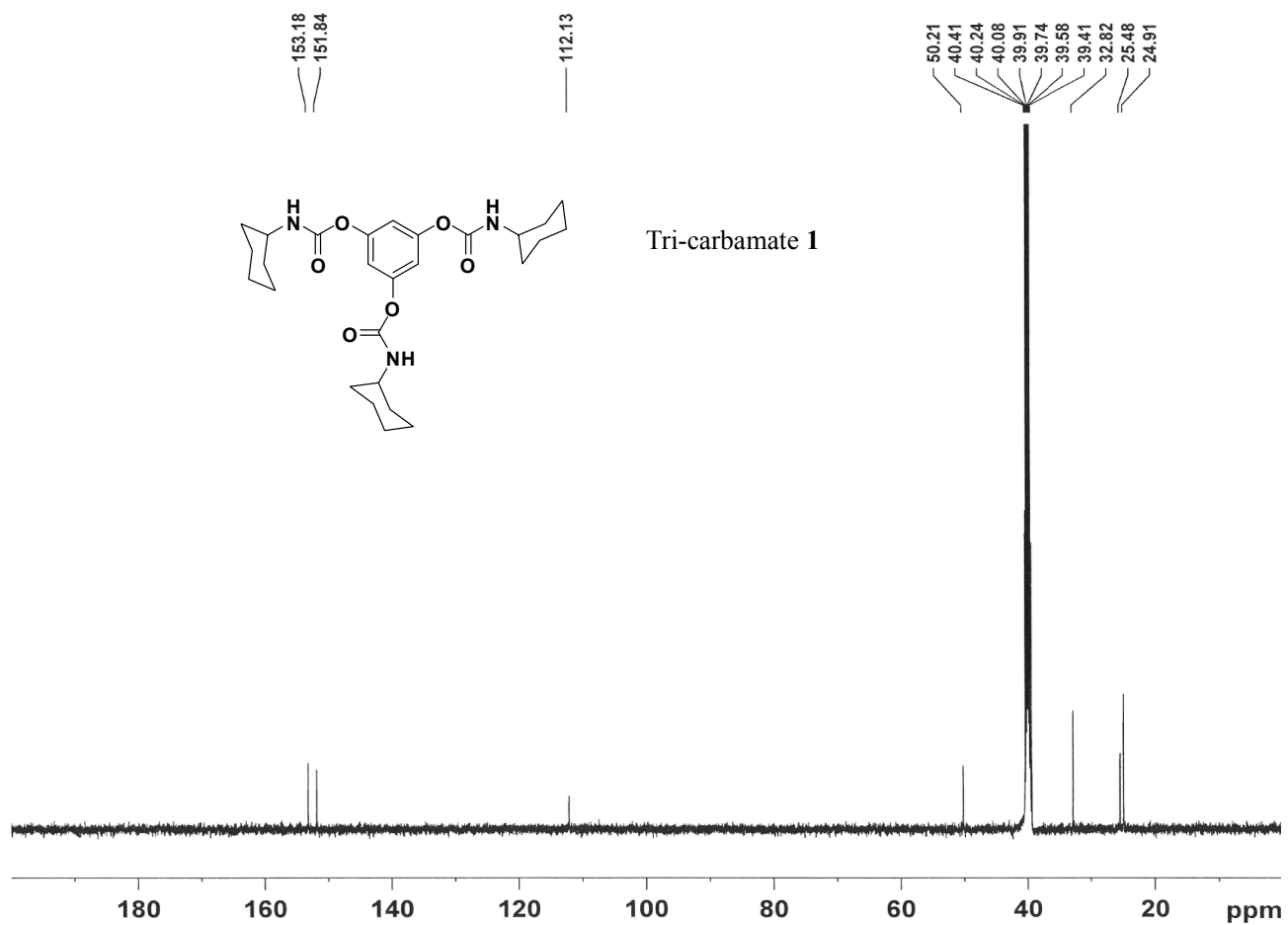


Fig. S6. ¹³C NMR spectrum of benzene-1, 3, 5-triyl tris(cyclohexylcarbamate) **1**.



Fig. S7. FT-IR spectrum of benzene-1,3,5-triyl tris(cyclohexylcarbamate) **1**.

RS S11-026 MeOH/ Amm. Acetate 5000v/100v

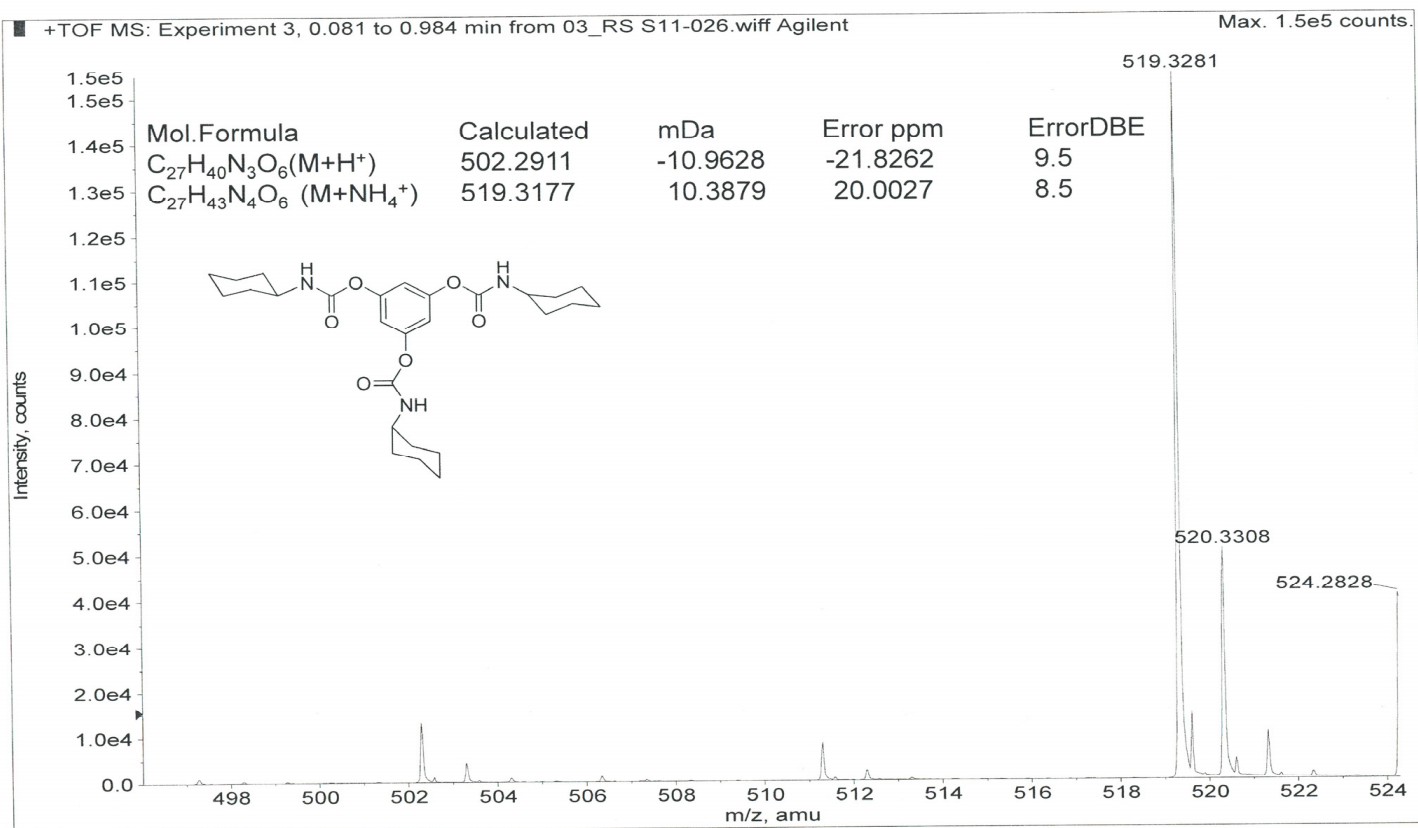


Fig. S8. HRMS spectrum of benzene-1, 3, 5-triyl tris(cyclohexylcarbamate) **1**.

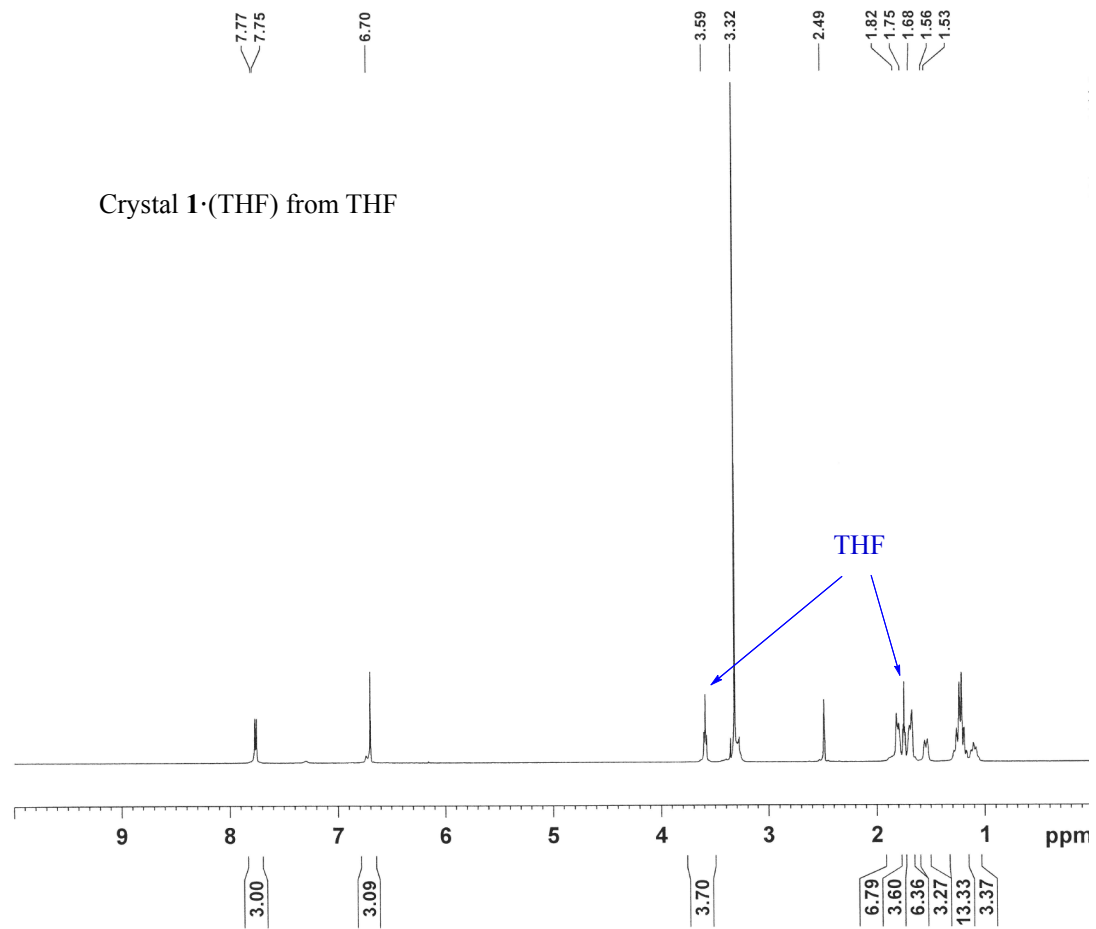


Fig. S9. ^1H NMR spectrum of **1**·(THF) crystals grown in wet THF containing 5% water.

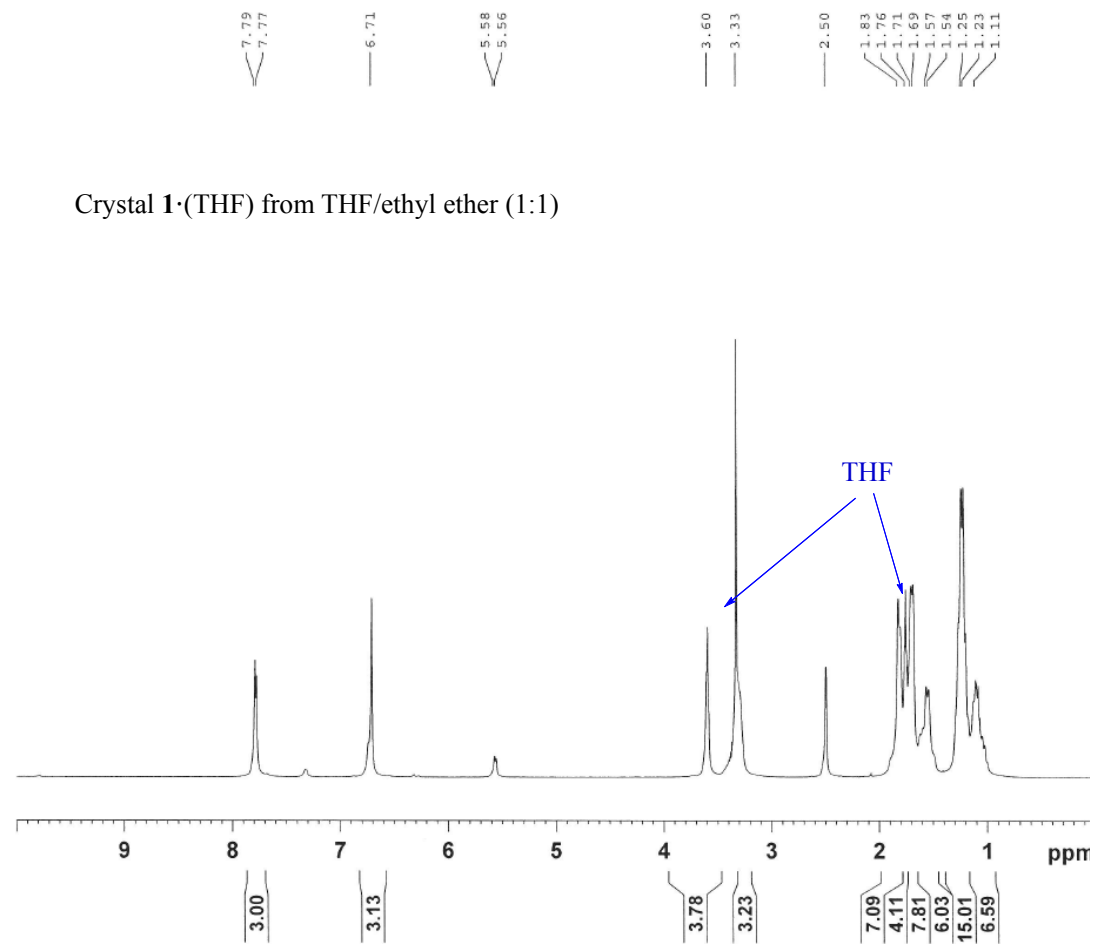


Fig. S10. ^1H NMR spectrum of **1**·(THF) crystals grown in a mixture solvent of THF/ethyl ether (1:1).

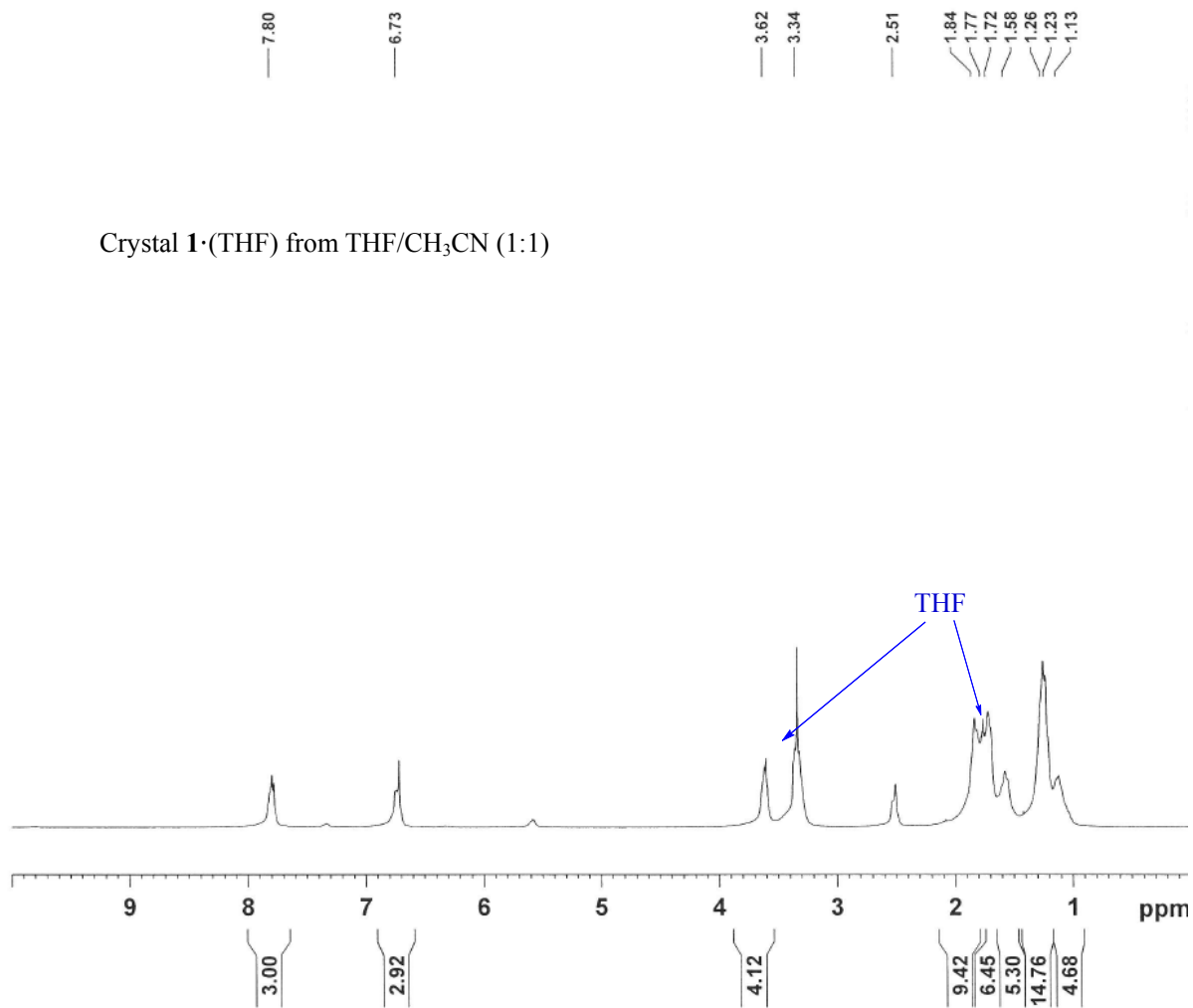


Fig. S11. ¹H NMR spectrum of **1**·(THF) crystals grown in a mixture solvent of THF/CH₃CN (1:1).

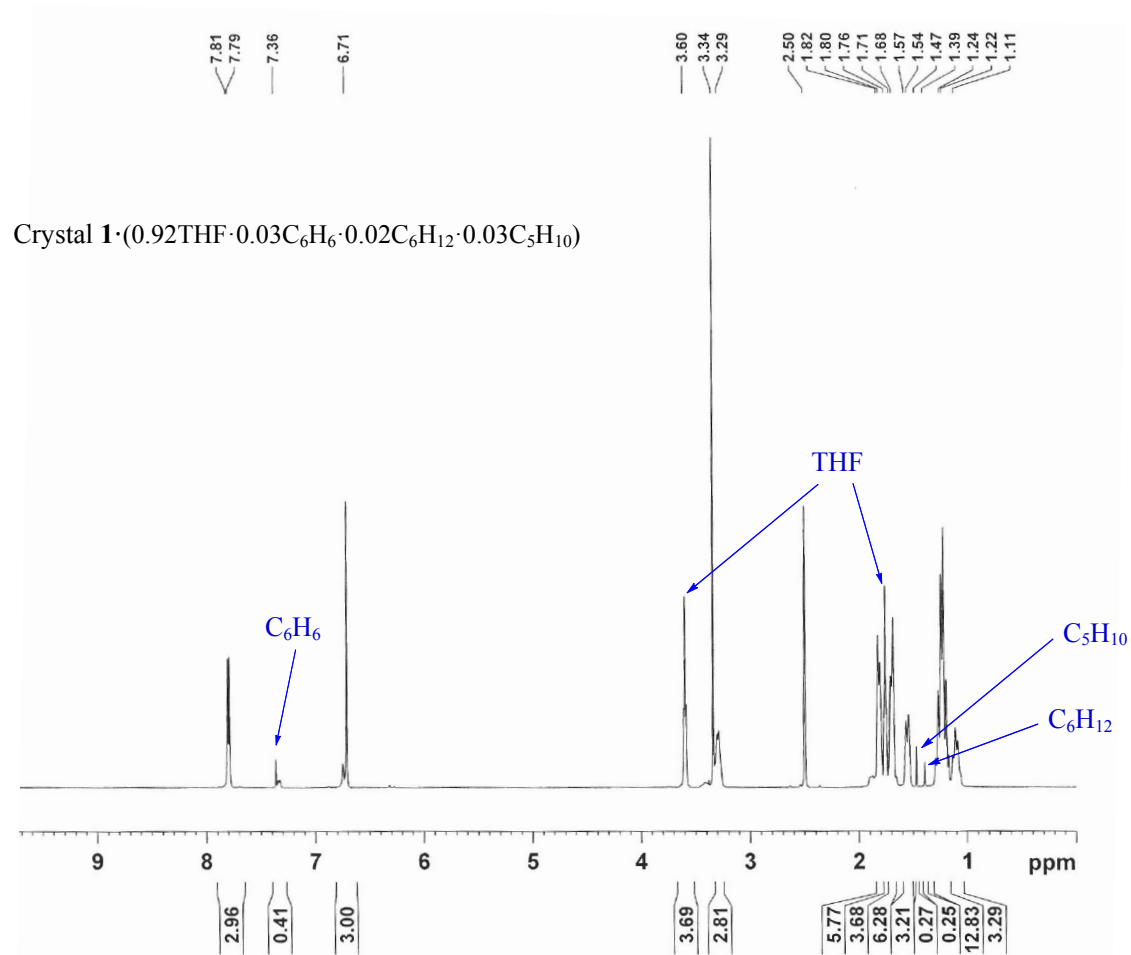


Fig. S12. ¹H NMR spectrum of benzene-1, 3, 5-triyl tris(cyclohexylcarbamate) **1** crystals grown in a mixture solvent of THF/benzene/cyclohexane/cyclopentane (1/1/1/1). Chemical shift of solvents (ppm): THF (3.60), benzene (7.37), cyclohexane (1.40) and cyclopentane (1.48). Selectivity of solvents: THF/benzene/cyclohexane/cyclopentane = 0.92:0.03:0.02:0.03

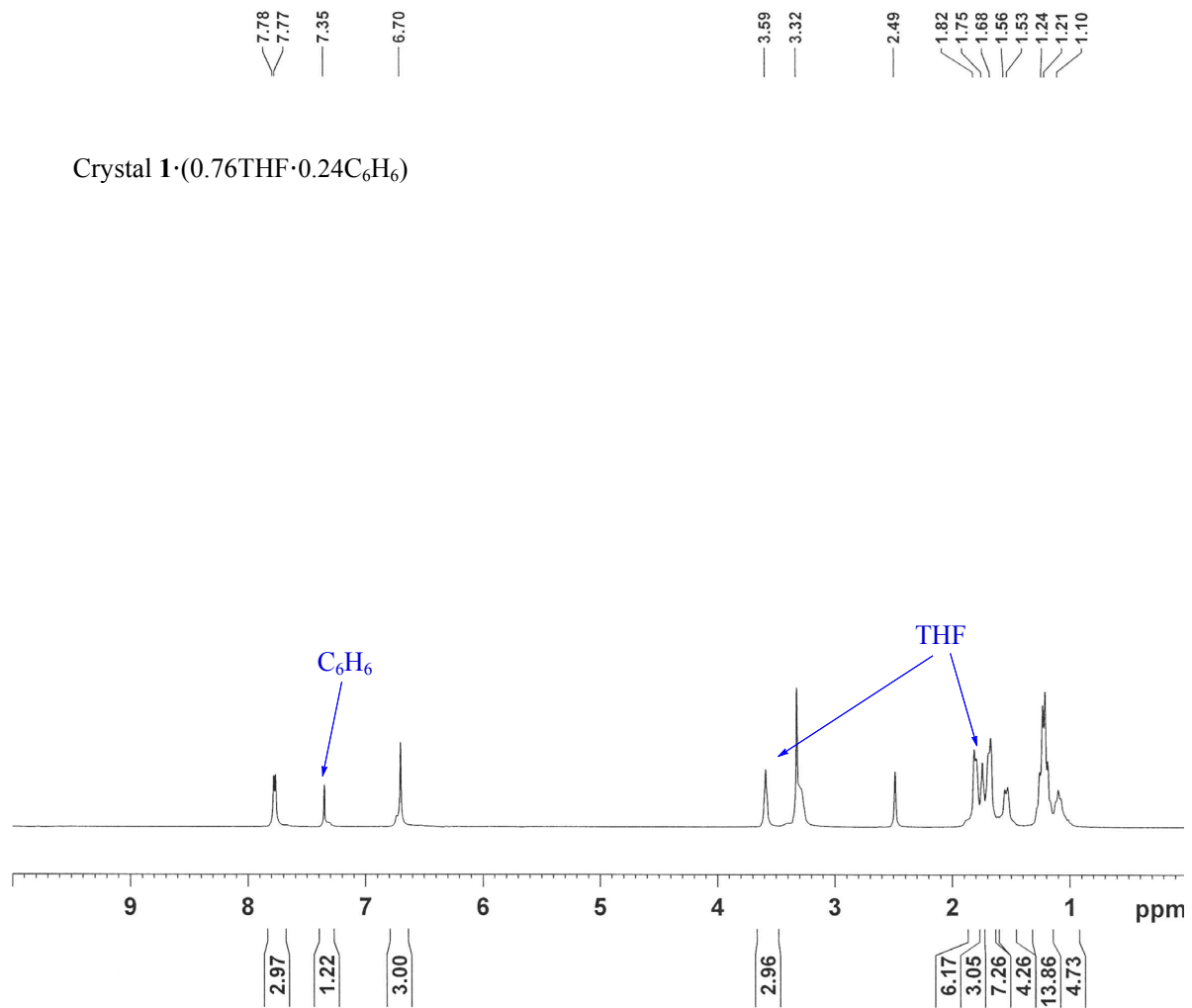
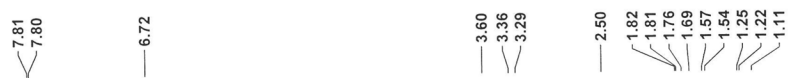


Fig. S13. ¹H NMR spectrum of benzene-1, 3, 5-triyl tris(cyclohexylcarbamate) **1** crystals grown in THF/benzene (1/1). Chemical shift of solvents (ppm): THF (3.60) and benzene (7.37). Selectivity of solvents: THF/benzene = ~ 0.76:0.24

Table S2. Desolvation and Absorption Experiments

Entry	Cycle	Time	Uptake (%)
1a	1 st	2 hours	85
1b	2 nd	overnight	83
1c	3 rd	15 min	50
2a	1 st	overnight	75
2b	2 nd	overnight	90
2c	3 rd	2 hours	80
2d	4 th	1 hours	72
3	1 st	2 days	100
4	1 st	overnight	80
5	1 st	1 hour	60

Note: Crystals grown in THF were desolvated by heating at 140 °C for 2 h, and the finish of desolvation was verified by ¹H NMR. The desolvated crystals were put in an air-tight vial. A small amount of nearly saturated THF solution of **1** was added with caution to protect the original shapes of the crystals from damage or dissolution. The crystals were dried in a fume hood for 0.5-2 h. The dried crystals were checked by NMR. Multiple parallel experiments have been conducted. An average 80% of THF molecules can be absorbed within 2h. Multiple cycles of absorption and desorption experiments showed that the capacity of the crystals of absorbed solvent molecules was not affected up to at least 4 times.



Entry 1a in Table S2.

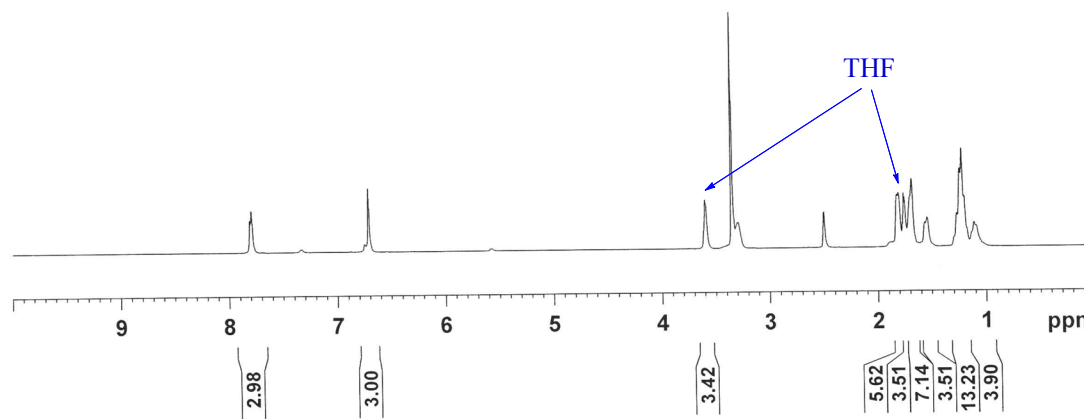


Fig. S14. Crystal **1**·(THF) from guest-free **1** by reabsorbing THF in 2 hours (Entry 1a in Table S2).

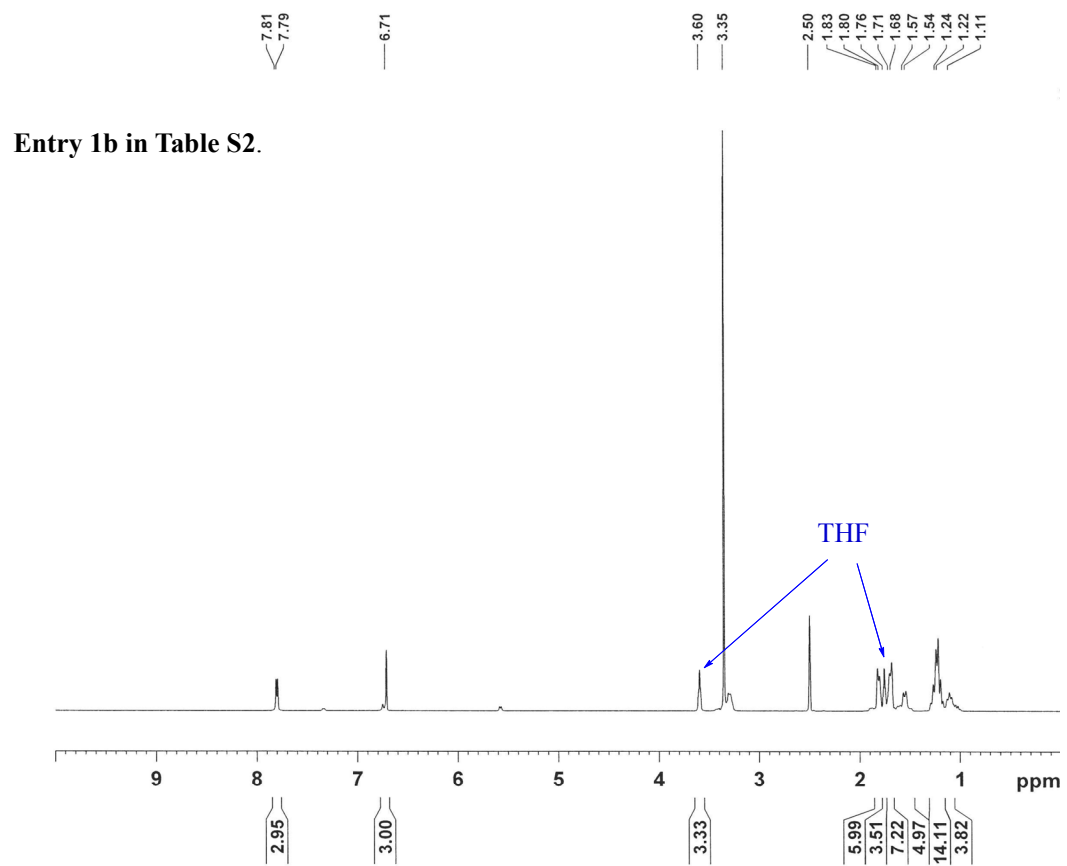


Fig. 15. Crystal 1·(THF) from guest-free 1 by reabsorbing THF in overnight (Entry 1b in Table S2).

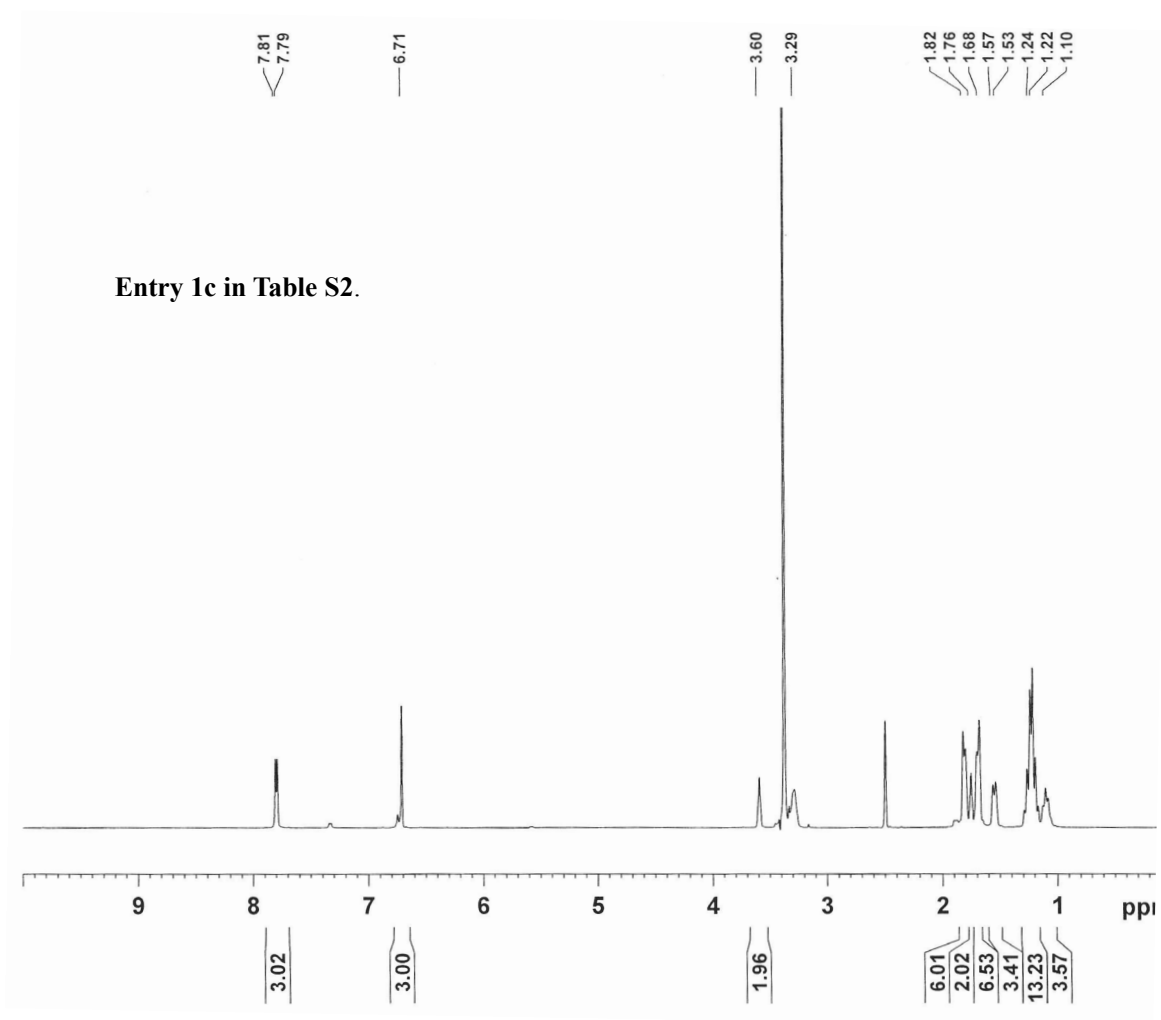
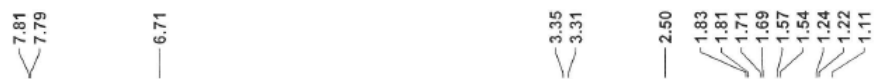


Fig. S16. Crystal **1**·(THF) from guest-free **1** by reabsorbing THF in 15 min (Entry 1c in Table S2).



Prepared Guest-free Crystals for Entry 2a in Table S2

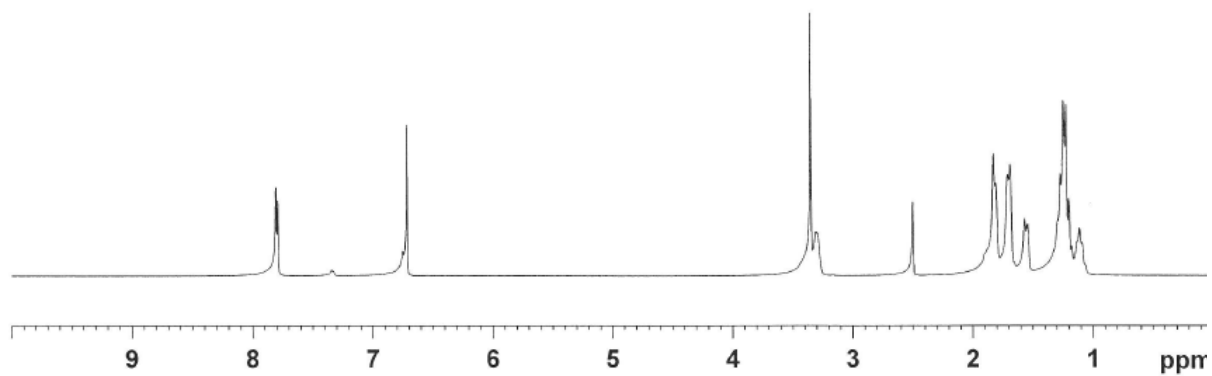
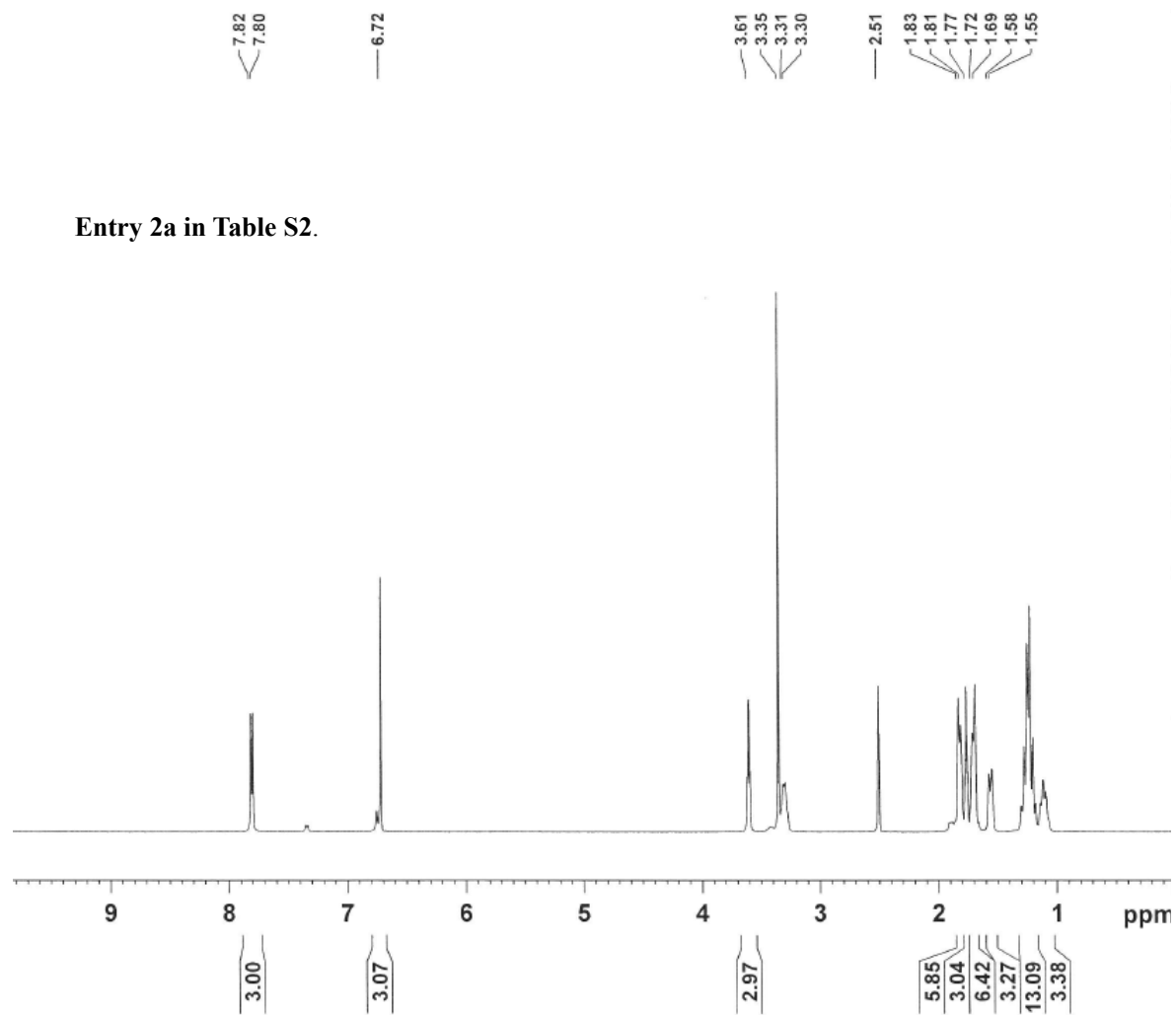


Fig. S17. Crystal 1 from Crystal 1·(THF) by heating at 140 °C for 2 h (Prepared Guest-free Crystals for Entry 2a in Table S2).



Entry 2a in Table S2.

Fig. S18. Crystal 1·(THF) from guest-free 1 by reabsorbing THF overnight (Entry 2a in Table S2).

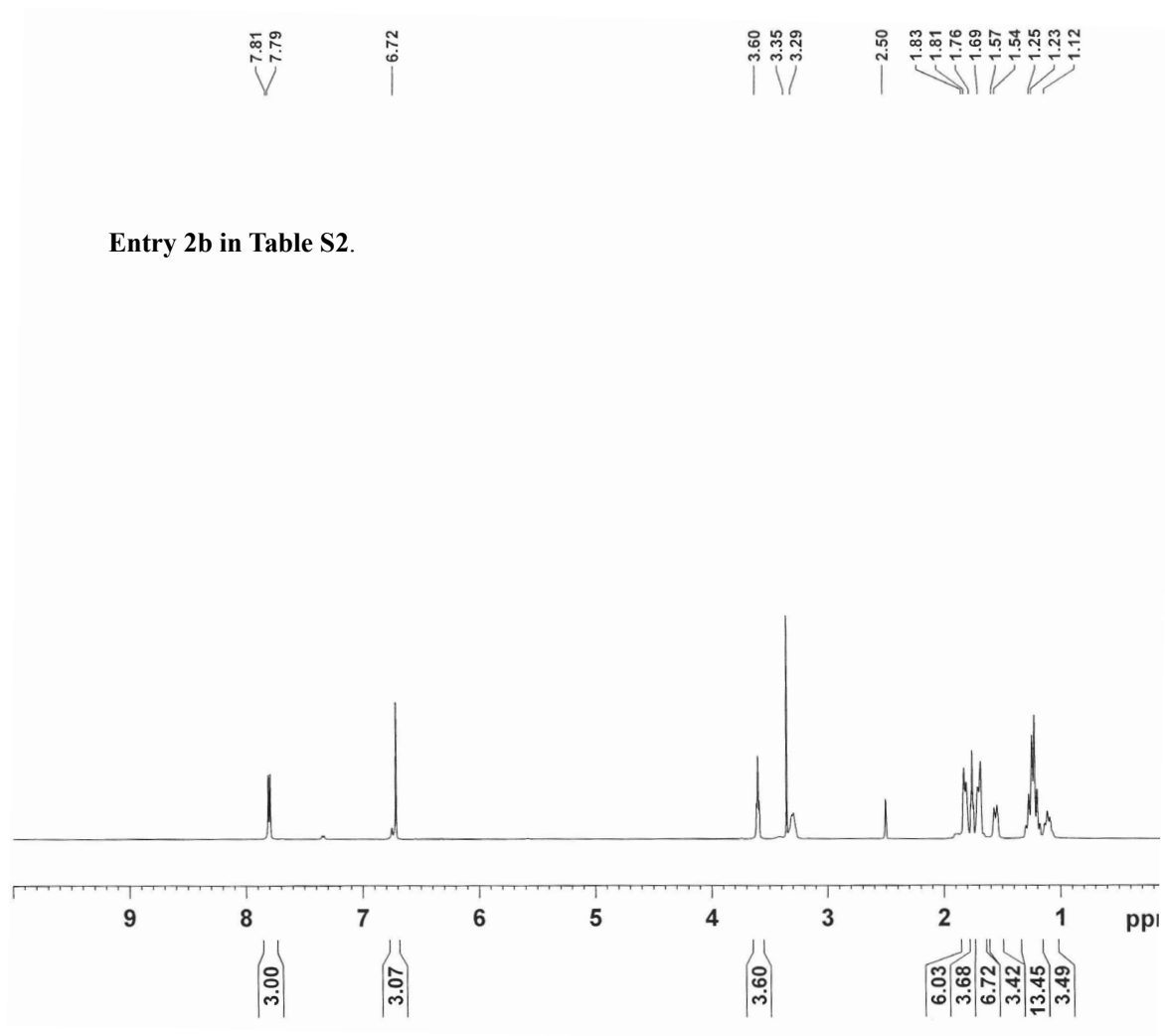
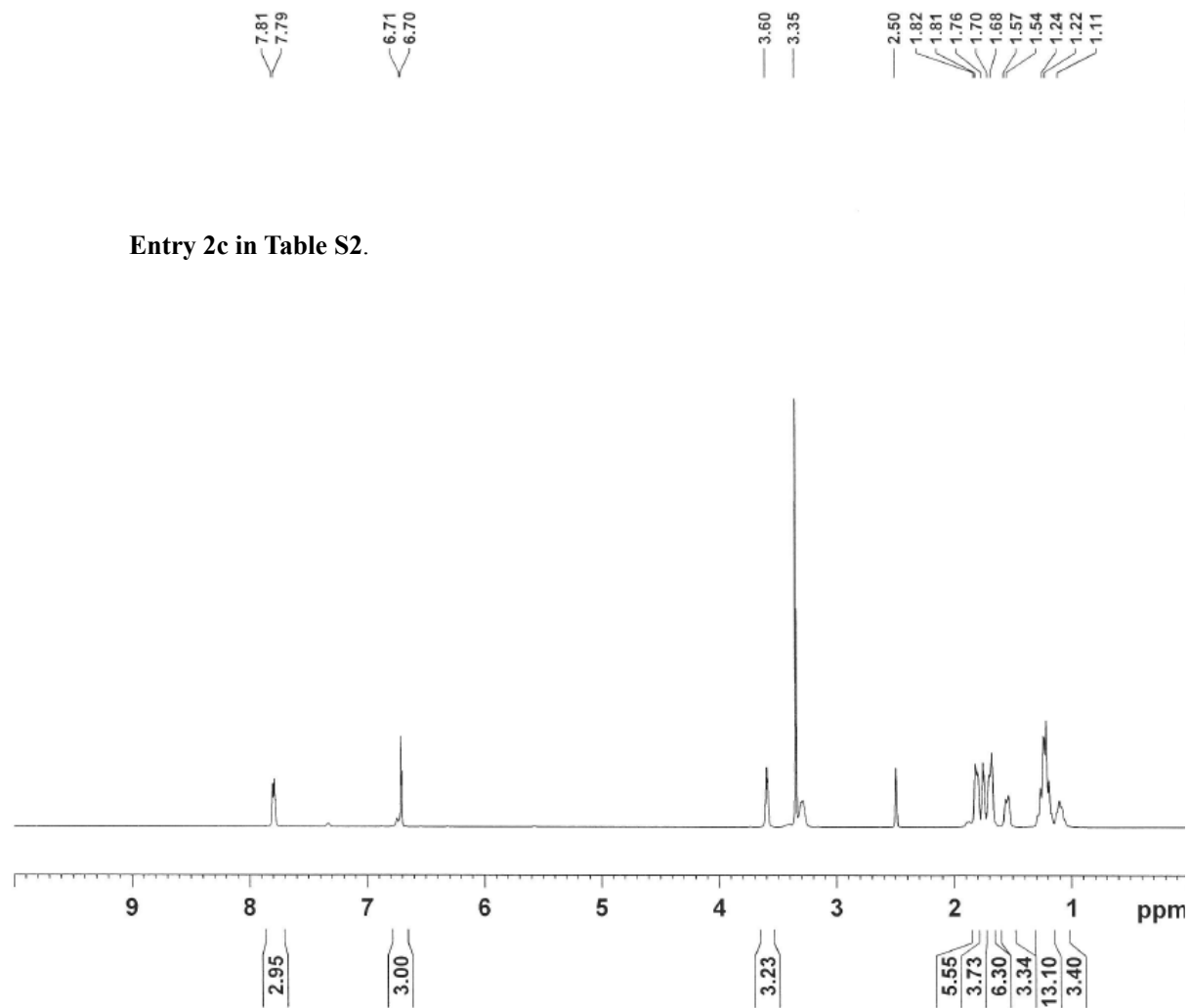


Fig. S19. Crystal 1·(THF) from guest-free **1** by reabsorbing THF overnight (Entry 2b in Table S2).



Entry 2c in Table S2.

Fig. S20. Crystal 1·(THF) from guest-free 1 by absorbing THF in 2 h (Entry 2c in Table S2).

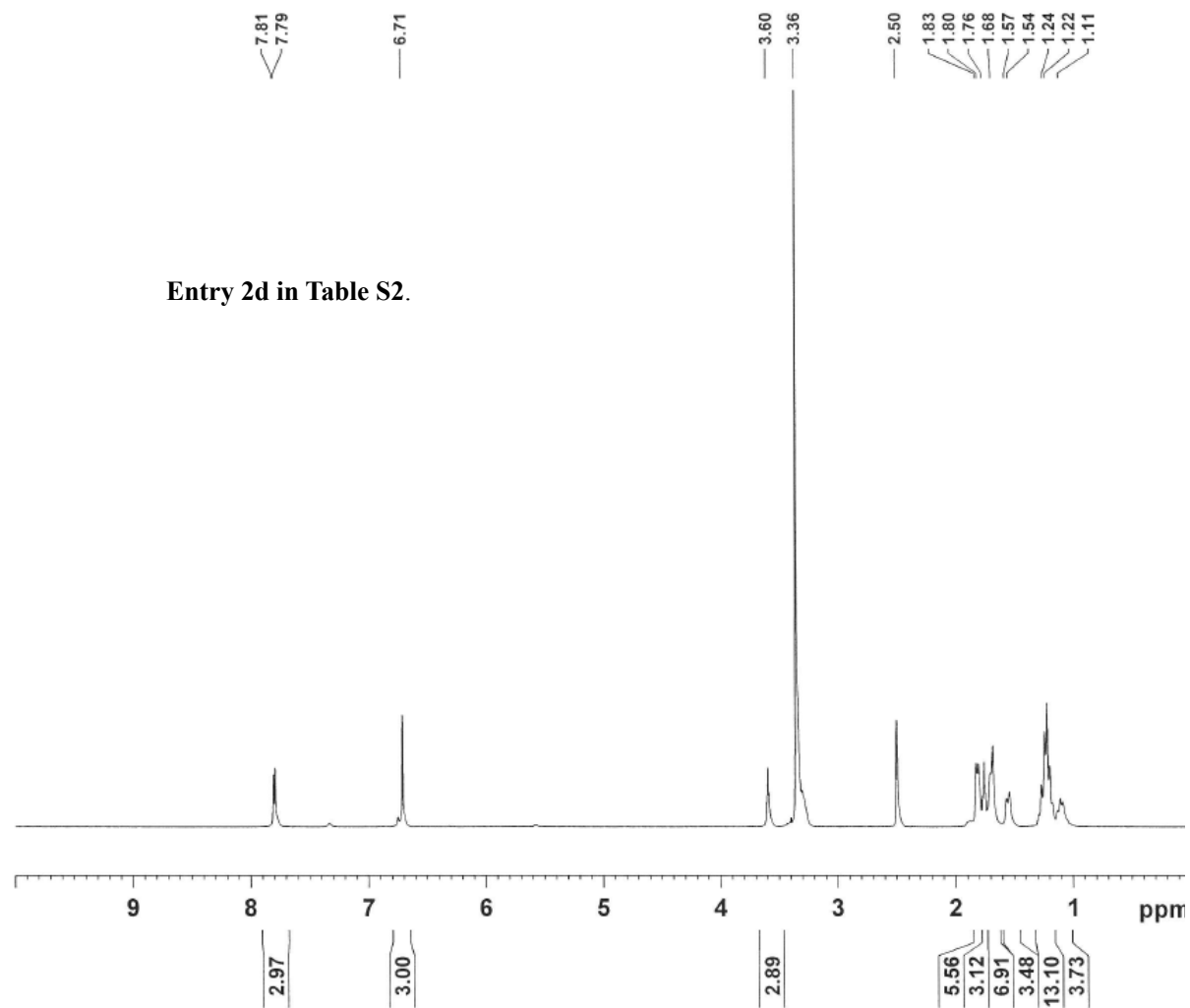


Fig. S21. Crystal **1**·(THF) from guest-free **1** by reabsorbing THF in 1 h (Entry 2d in Table S2).



Entry 3 in Table S2.

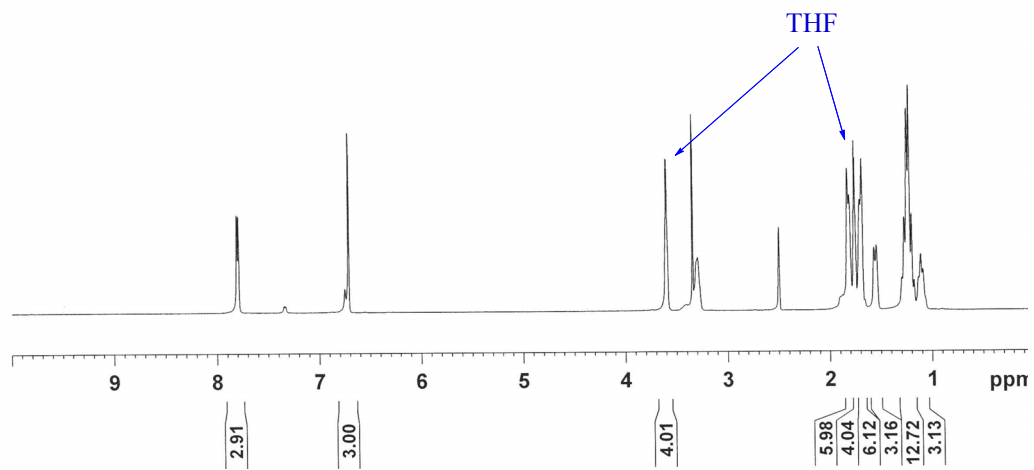
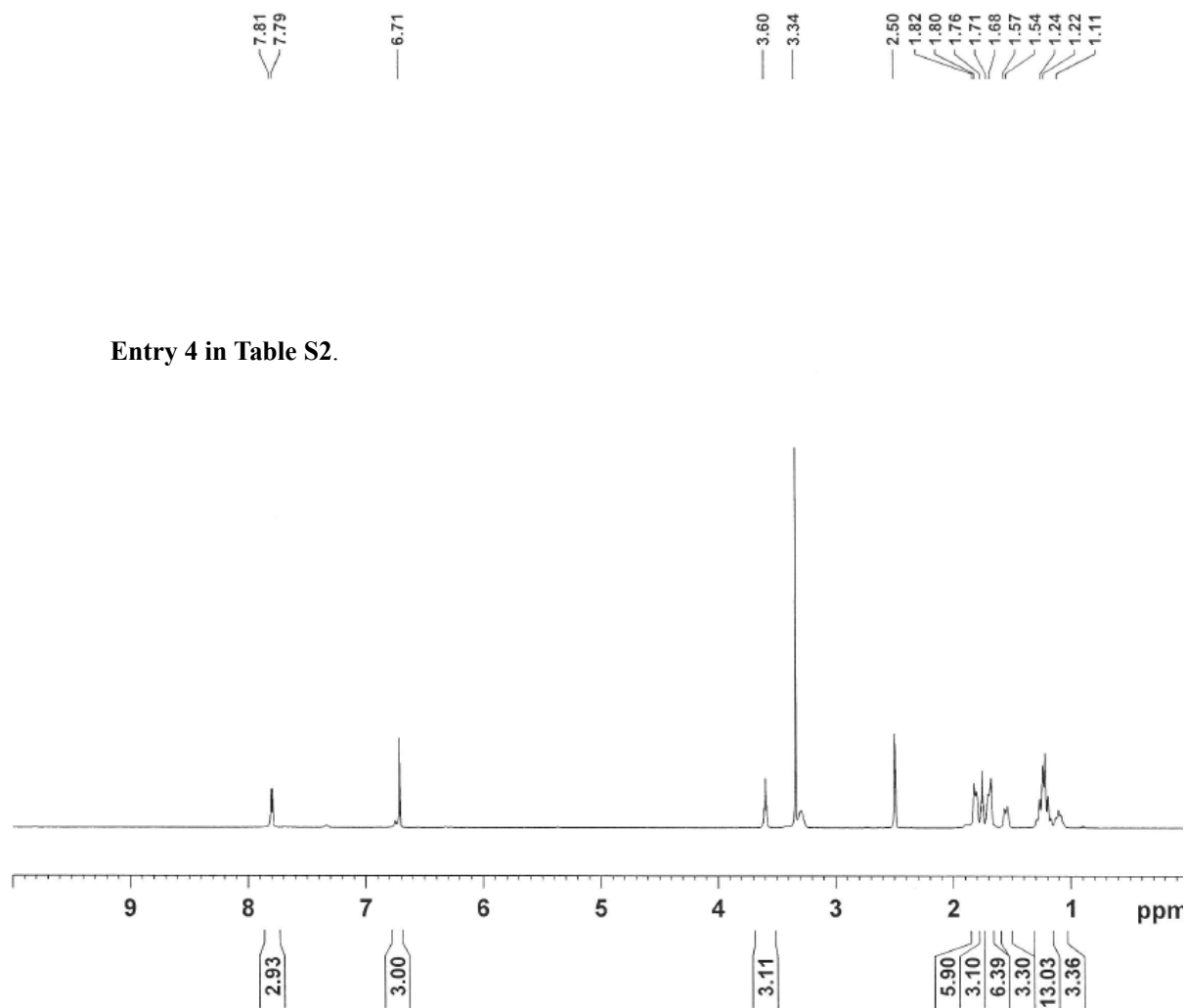
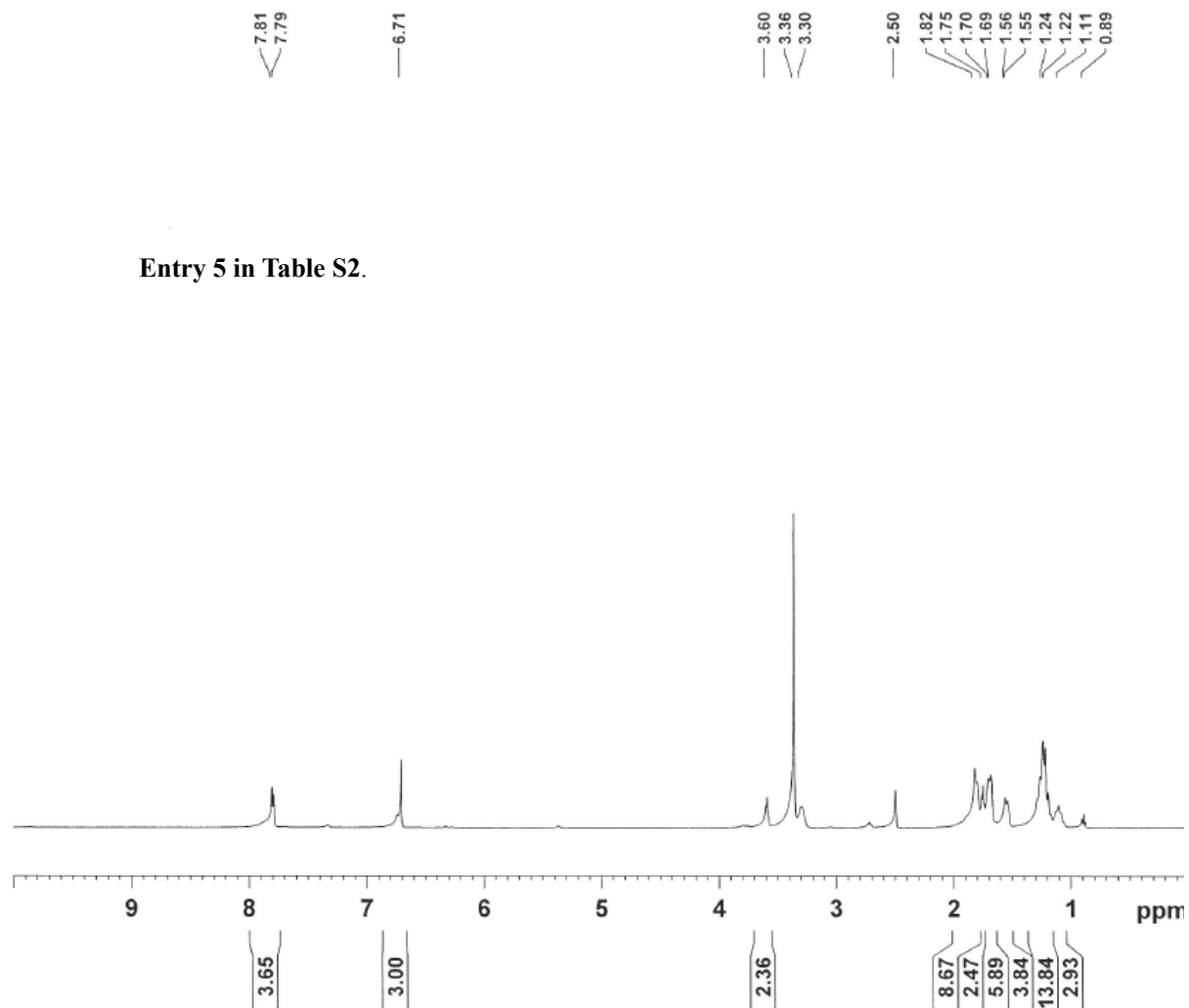


Fig. S22. Crystal 1·(THF) from guest-free 1 by reabsorbing THF in two days (Entry 3 in Table S2).



Entry 4 in Table S2.

Fig. S23. Crystal 1·(THF) from guest-free 1 by reabsorbing THF overnight (Entry 4 in Table S2).



Entry 5 in Table S2.

Fig. S24. Crystal 1·(THF) from guest-free **1** by reabsorbing THF in 1 h (Entry 5 in Table S2).

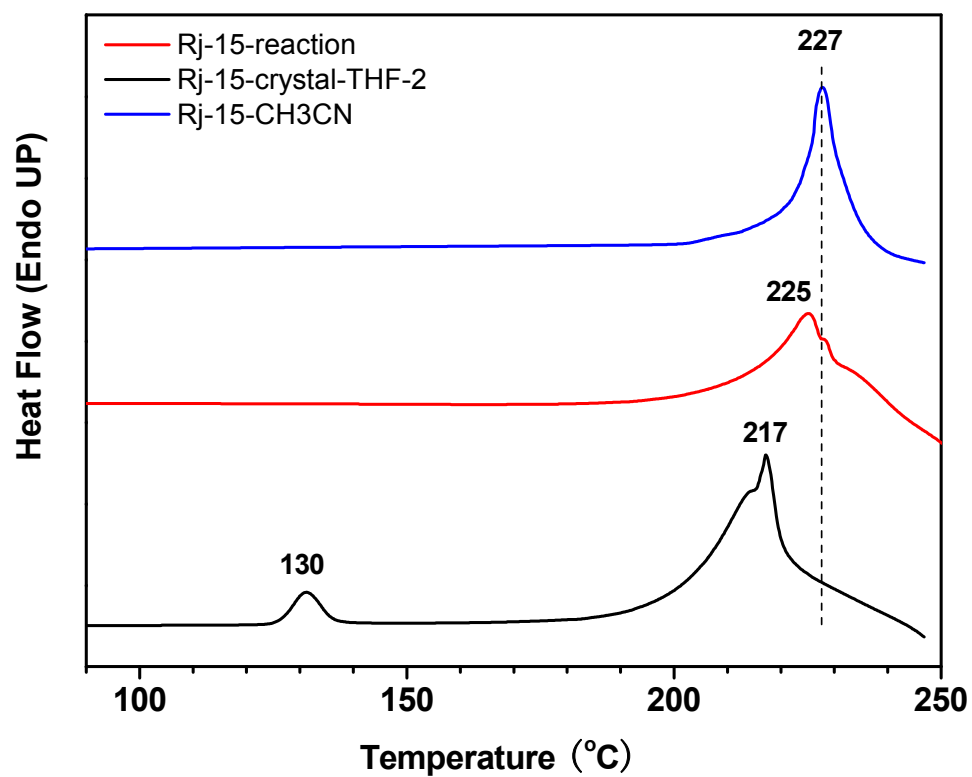


Fig. S25. DSC Curves of Benzene-1, 3, 5-triyl tris(cyclohexylcarbamate) **1** and **1**·(THF): (Blue) single crystals **1** grown in CH₃CN solution; (Red) powder of **1** obtained directly from the synthesis without further processing; (Black) fresh crystals **1**·(THF) obtained by the slow evaporation of wet THF solution.