Electronic Supplementary Information

For

Uranyl dication mediated photoswitching of a calix[4]pyrrole-based metal coordination cage

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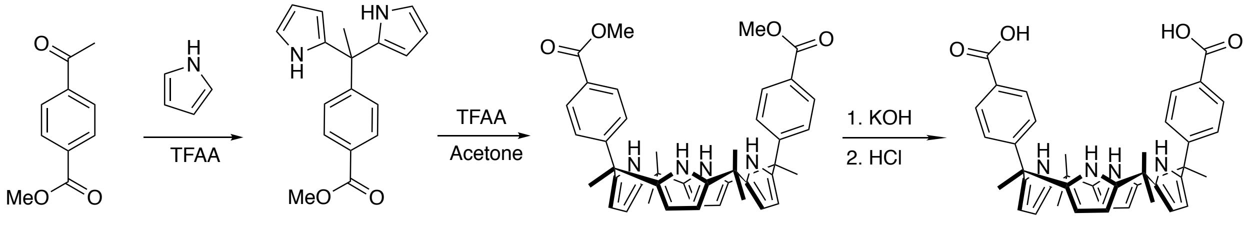

2 **3** **4** **1**

All solvents and chemicals used were purchased from Aldrich, TCI, or Acros and used without further purification. NMR spectra were recorded on a Varian Mercury 400 MHz instrument. The NMR spectra were referenced to solvent and the spectroscopic solvents were purchased from either Cambridge Isotope Laboratories or Aldrich Chemical Co. Chemical ionization (CI) mass spectra were recorded on a VG ZAB-2E instrument. Electrospray ionization mass spectrometry (ESI-MS) was carried out on a VG AutoSpec apparatus (chemical precursors) or a Waters Synapt G-2 instrument (cage complexes). Sorbent Technologies silica gel (200 nm) sheets were used for TLC analyses. Column chromatography was performed on Sorbent silica gel 60 (40-63 mm).

Compound **3**

To methyl 4-acetylbenzoate (**2**) (5.66 g, 31.76 mmol) in pyrrole (300 mL) was added TFAA (trifluoroacetic anhydride, 2.5 mL, 17.98 mmol). The mixture was stirred for 10 hours at 60 °C. The resulting solution was evaporated in vacuo to remove pyrrole and other volatiles. The material obtained in this way was purified by column chromatography over silica gel (eluent: dichloromethane) to afford a pale-yellow oil. Repeated addition of 25 mL hexanes: dichloromethane (1:1, v/v) followed by removal of solvent in vacuo until solid was followed by washing with hexanes and filtering. This gave 8.36 g (89% yield) of **3** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95-7.92 (d, 2H, Ar*H*), 7.80 (br s, 2H, pyrrole-N*H*), 7.20-7.18 (d, 2H, Ar*H*), 6.71-6.69 (m, 2H, Ar*H* (pyrrole)), 6.19-6.17 (m, 2H, Ar*H* (pyrrole)), 5.97-5.95 (m, 2H, Ar*H* (pyrrole)), 3.90 (s, 3H, C*H$_3$*), 2.06 (s, 3H, C*H$_3$*). ^{13}C NMR (100 MHz, CDCl$_3$): δ 167.1, 152.7, 136.7, 129.6, 128.7, 127.6, 117.4, 108.5, 106.7, 52.3, 45.1, 28.7. HRMS (ESI) *m/z* 295.14450 [M + H]$^+$ calcd for $C_{18}H_{18}N_2O_2$ found 295.14410.

Compound **4**

To a mixture of compound **3** (5.91 g, 20.09 mmol) and methanol/acetone (1:1, 300 mL), TFAA (trifluoroacetic anhydride, 1.42 mL, 10.00 mmol) was added at 0 °C and stirred for 1 hour. The solution was then stirred for 10 hours at room temperature and quenched with triethylamine. The resulting solution was evaporated in vacuo and re-dissolved in dichloromethane, washed with brine, and dried over Na_2SO_4. Column chromatography over silica gel (ethyl acetate/hexanes = 1/9) gave compound **4** (578 mg, 9% yield) as white solids. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.90-7.88 (d, 4H, Ar*H*), 7.24 (br s, 4H, pyrrole N*H*), 7.05-7.03 (d, 4H, Ar*H*), 5.94-5.92 (t, 4H, Ar*H* (pyrrole)), 5.61-5.59 (t, 4H, Ar*H* (pyrrole)), 3.89 (s, 6H, C*H$_3$*), 1.90 (s, 6H, C*H$_3$*), 1.63 (s, 6H, C*H$_3$*), 1.53 (s, 6H, C*H$_3$*). ^{13}C NMR (100 MHz, CDCl$_3$): δ 167.1, 153.2, 138.7, 136.0, 129.1, 128.5, 127.6, 106.3, 103.5, 52.2, 45.0, 35.3, 30.2, 27.9, 27.7. HRMS (ESI) *m/z* 669.34350 (M + H)$^+$ calcd for $C_{42}H_{45}N_4O_4$, found 669.34450.

Compound **1**

A mixture of compound **4** (578 mg, 0.90 mmol) and KOH (1.5 g, 27.00 mmol) in H_2O/2-propanol (1:1, 100 mL) was heated at reflux for 1 hour. The reaction was cooled to room temperature and then further cooled to 0 °C. The solution was acidified with hydrochloric acid until it reached pH = 2. The white precipitate obtained in this way was filtered and washed with water until the washings were neutral. The resulting solid was dried in the air to give compound **1** (547 mg, 95% yield). ^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 12.79 (br s, 2H, COO*H*), 9.64 (s, 4H, pyrrole N*H*), 7.84-7.82 (d, 4H, Ar*H*), 7.00-6.98 (d, 4H, Ar*H*), 5.76-5.61 (d, 8H, Ar*H* (pyrrole)), 1.83 (s, 6H, C*H$_3$*), 1.63 (s, 6H, C*H$_3$*), 1.50 (s, 6H, C*H$_3$*). ^{13}C NMR (100 MHz, DMSO-*d*$_6$): δ 167.3, 155.0, 139.6, 136.0, 129.0, 127.1, 105.1, 102.1, 44.5, 34.7, 30.9, 29.2, 27.8. HRMS (ESI) *m/z* 641.31210 $(M + H)^+$ calcd for $C_{40}H_{40}N_4O_4$, found 641.31220.

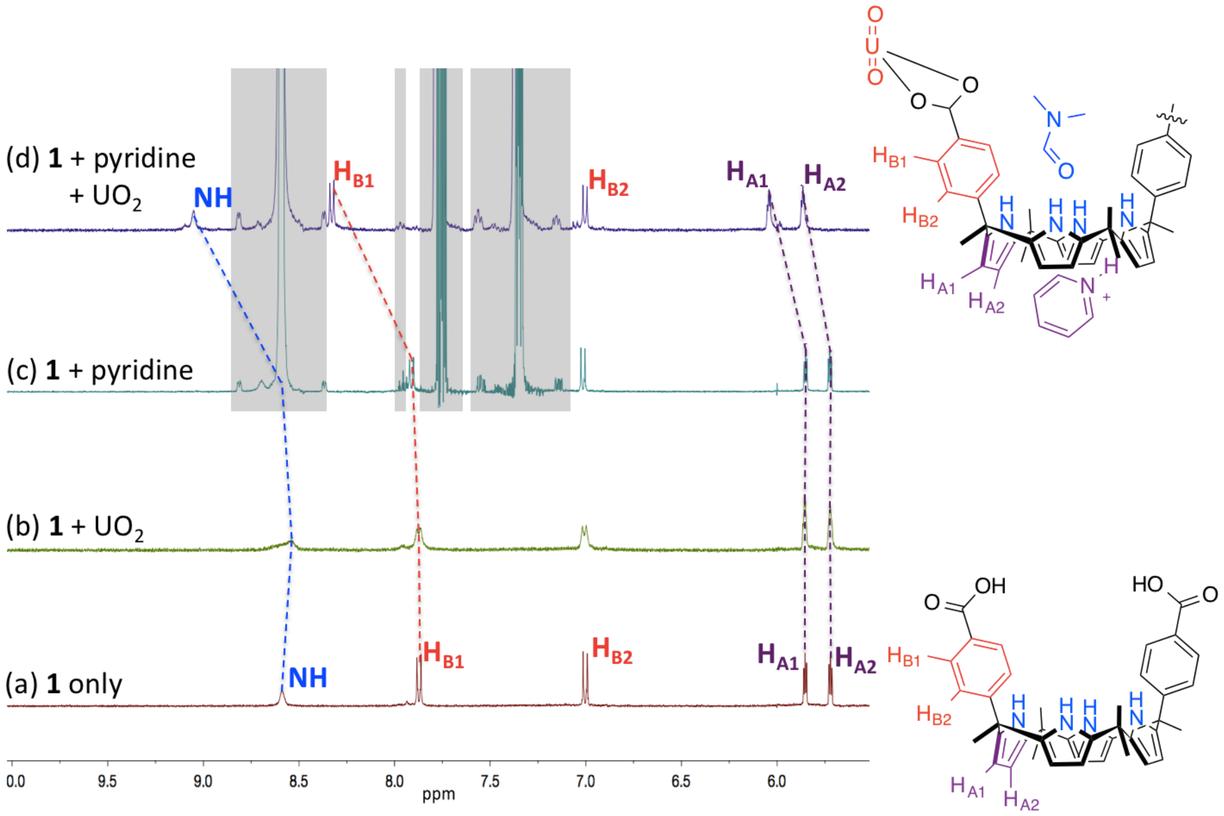

Figure S1. Partial ^{1}H NMR spectrum of (a) **1** only (3.75 mM), (b) **1** + 0.66 equiv. of $UO_2(NO_3)_2 \cdot 6H_2O$, (c) **1** + 82.74 equiv. of pyridine, and (d) **1** + 0.66 equiv. of $UO_2(NO_3)_2 \cdot 6H_2O$ + 82.74 equiv. of pyridine, recorded at room temperature in CD_3CN (1.5% DMF-*d*$_7$). Shaded regions are highlighted to aid in visualization of the aromatic proton peaks ascribed to pyridine.

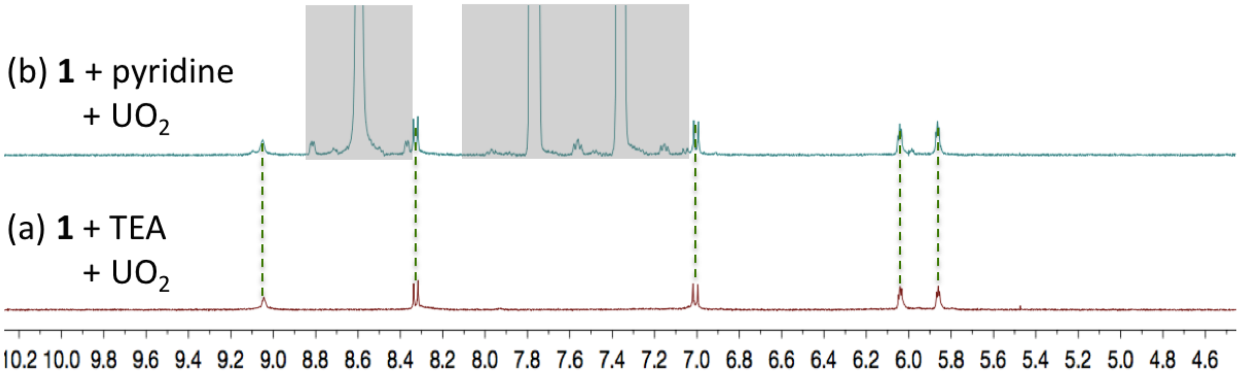

Figure S2. Stacked arrangement of selected portions of the ^{1}H NMR spectra of (a) **1** (3.75 mM) + 0.66 equiv. of $UO_2(NO_3)_2\cdot 6H_2O$ + 38.22 equiv. of TEA and (b) **1** + 0.66 equiv. of $UO_2(NO_3)_2\cdot 6H_2O$ + 82.74 equiv. of pyridine, recorded at room temperature in CD_3CN (1.5% DMF-*d*$_7$). Shaded regions are highlighted to aid in visualization of the aromatic proton peaks ascribed to pyridine.

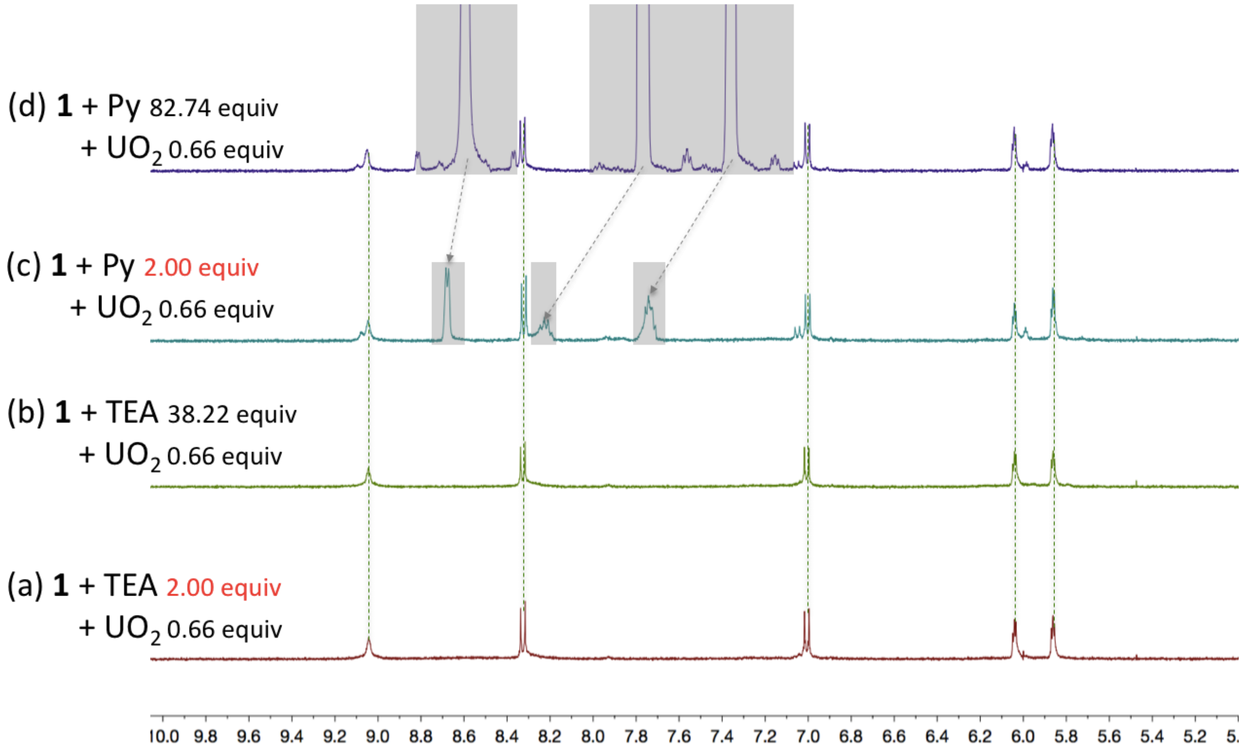

Figure S3. Stacked arrangement of selected portions of the ^{1}H NMR spectra of (a) **1** (3.75 mM) + 0.66 equiv. of $UO_2(NO_3)_2 \cdot 6H_2O$ + 2.00 equiv. of TEA**,** (b) **1** + 0.66 equiv. of $UO_2(NO_3)_2 \cdot 6H_2O$ + 38.22 equiv. of TEA, (c) **1** + 0.66 equiv. of $UO_2(NO_3)_2 \cdot 6H_2O$ + 2.00 equiv. of pyridine, and (d) **1** + 0.66 equiv. of $UO_2(NO_3)_2 \cdot 6H_2O$ + 82.74 equiv. of pyridine, recorded at room temperature in CD_3CN (1.5% DMF-*d*$_7$). Shaded regions are highlighted to aid in visualization of the aromatic proton peaks ascribed to pyridine.

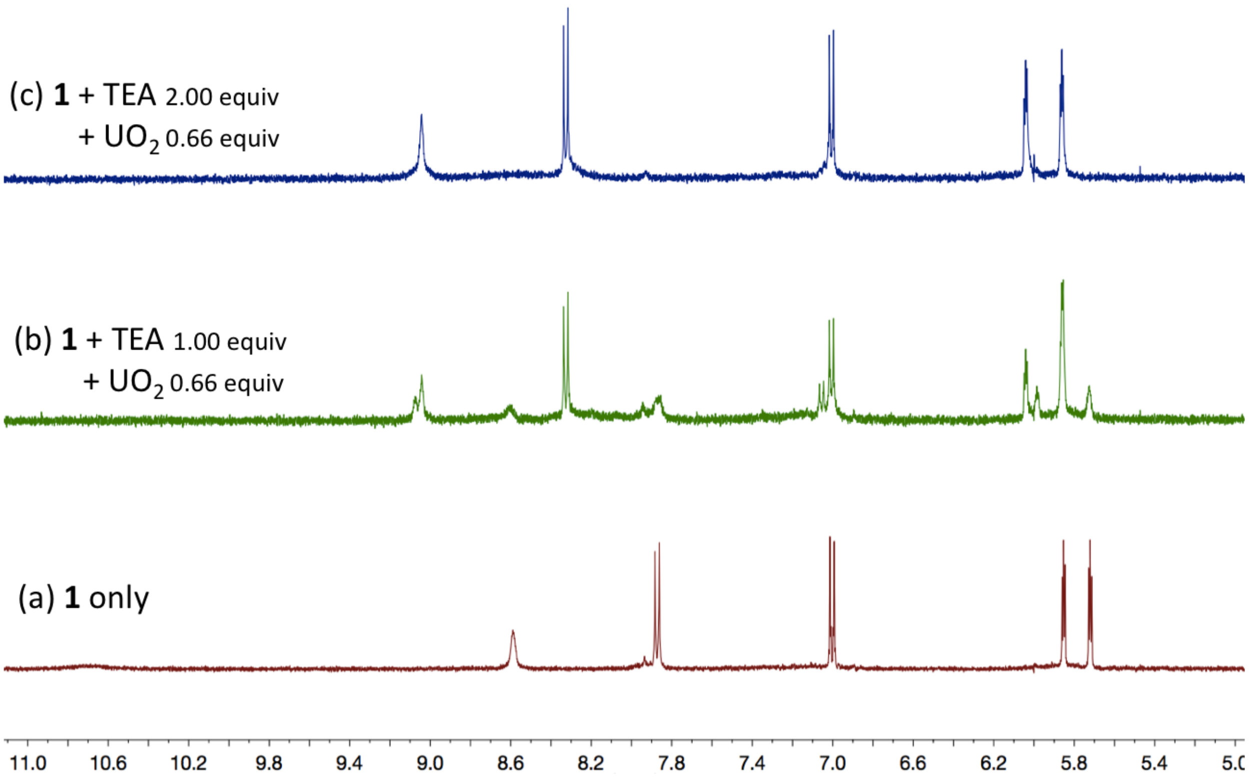

Figure S4. Partial ^{1}H NMR spectra of (a) **1** only (3.75 mM), (b) **1** + 0.66 equiv. of $UO_2(NO_3)_2 \cdot 6H_2O$ + 1.00 equiv. of TEA, and (c) **1** + 0.66 equiv. of $UO_2(NO_3)_2 \cdot 6H_2O$ + 2.00 equiv. of TEA, recorded at room temperature in CD_3CN (1.5% DMF-d_7).

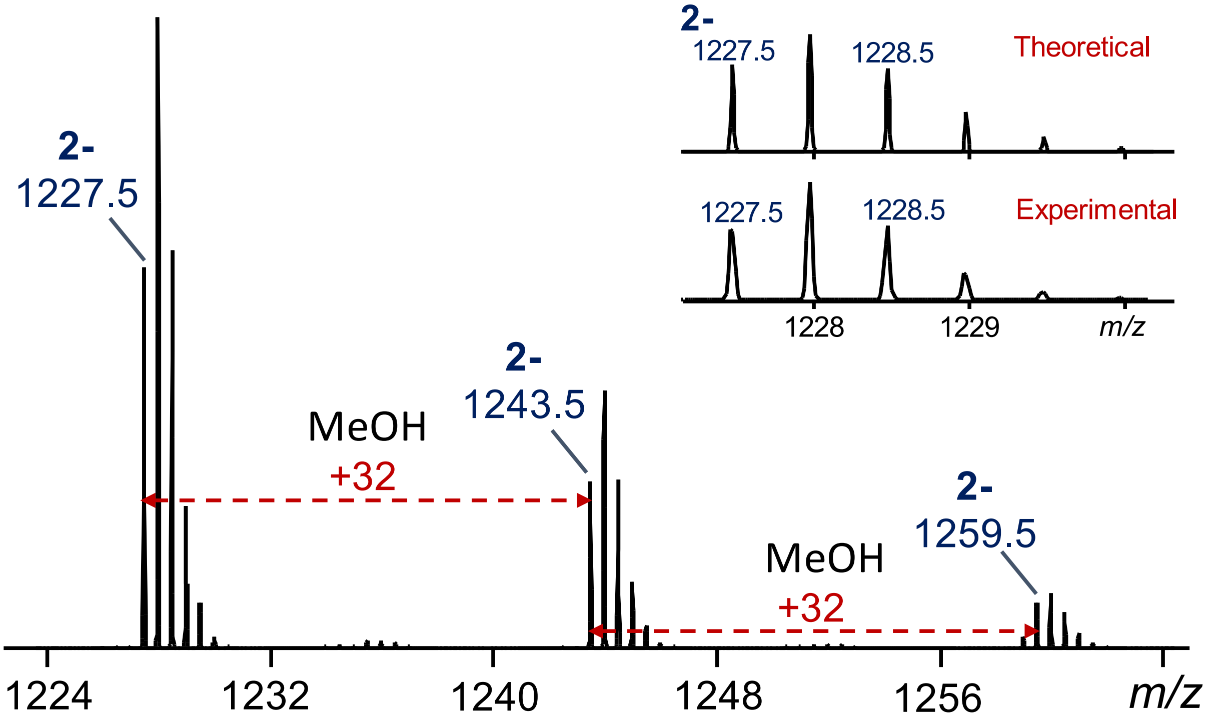

Figure S5. ESI-MS of **cage-1**. The experiments were performed under the following conditions: ESI capillary voltage, 3.0 kV; sample cone voltage, 30 V; extraction cone voltage, 3.0 V; source temperature 80°C; desolvation temperature, 100 °C; cone gas flow, 10 L/h; desolvation gas flow, 700 L/h (N_2)

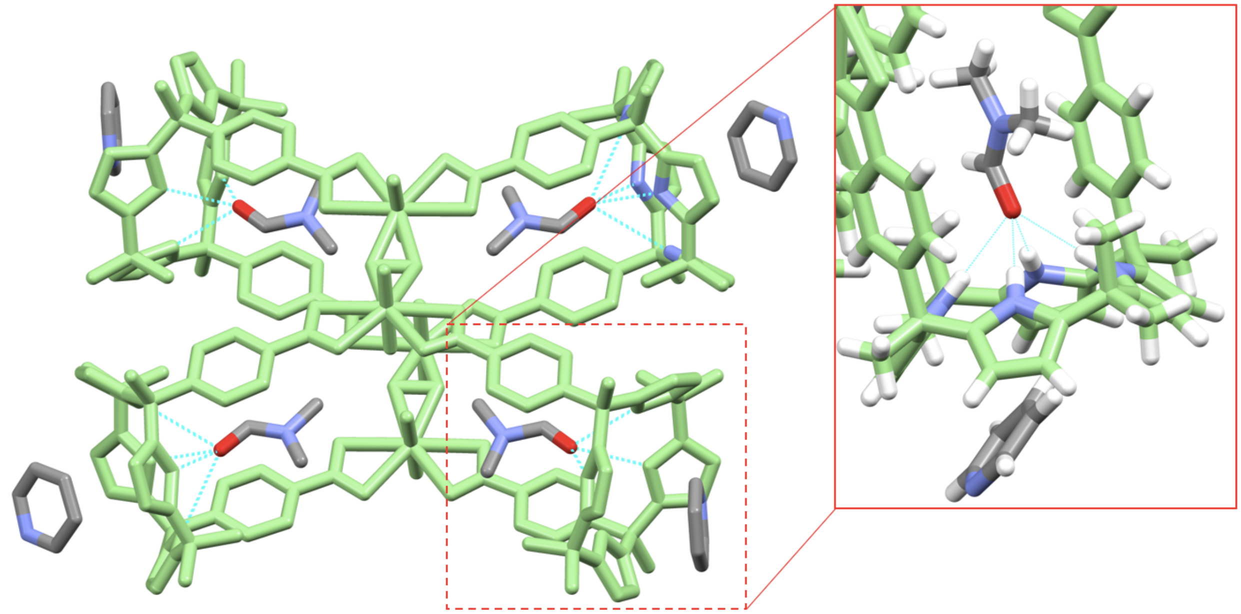

Figure S6. Crystal structure of **cage-2** with DMF molecules that, based on the metric parameters, are considered hydrogen bond to pyrrolic NH protons of calix[4]pyrrole ligands. The cage structure has been colored light green for clarity.

X-ray Experimental for complex for 1

Crystals grew as long, colorless laths by slow evaporation from acetonitrile. The data crystal was cut from a larger crystal and had approximate dimensions; 0.44 x 0.082 x 0.034 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a μ-focus Cu Kα radiation source ($\lambda = 1.5418$ Å) with collimating mirror monochromators. A total of 1445 frames of data were collected using ω-scans with a scan range of 1° and a counting time of 7.5 seconds per frame with a detector offset of +/- 40.1° and 30 seconds per frame with a detector offset of +/- 108.9°. The data were collected at 100 K using an Oxford 700 Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table S1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.39.46.[1] The structure was solved by direct methods using SHELXT[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.[3] Structure analysis was aided by use of the programs PLATON[4] and WinGX.[5] The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

Refined as a 2-component twin. The twin law was determined using CrysAlisPro. A small peak was observed within H-bonding distance to two pyrrole groups of the calixpyrrole on the side opposite O49. It was nestled in a gap between adjacent calixpyrrole molecules. The peak was assigned to be an oxygen atom as it was likely due to the presence of a small amount of water. The isotropic displacement parameter for this atom, O1w, was fixed while refining its site occupancy factor.

The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.101*P)^2 + (0.9446*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.169, with R(F) equal to 0.0565 and a goodness of fit, S, = 1.02. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[6] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[7] All figures were generated using SHELXTL/PC.[8] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found in the CIF. CCDC deposition number: 1850738.

Table S1. Crystal data and structure refinement for **1**.

Empirical formula	C44 H48 N6 O5	
Formula weight	740.88	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.1805(4) Å	α = 71.554(4)°.
	b = 12.0077(6) Å	β = 78.981(3)°.
	c = 16.8416(6) Å	γ = 68.315(4)°.
Volume	1985.98(16) $Å^3$	
Z	2	
Density (calculated)	1.239 Mg/m^3	
Absorption coefficient	0.659 mm^{-1}	
F(000)	788	
Crystal size	0.440 x 0.082 x 0.034 mm^3	
Theta range for data collection	2.776 to 74.659°.	
Index ranges	-13<=h<=13, -14<=k<=10, -20<=l<=18	
Reflections collected	7732	
Independent reflections	7732	
Completeness to theta = 67.684°	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.767	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7732 / 0 / 513	
Goodness-of-fit on F^2	1.015	
Final R indices [I>2sigma(I)]	R1 = 0.0565, wR2 = 0.1586	
R indices (all data)	R1 = 0.0759, wR2 = 0.1687	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.428 and -0.295 e.$Å^{-3}$	

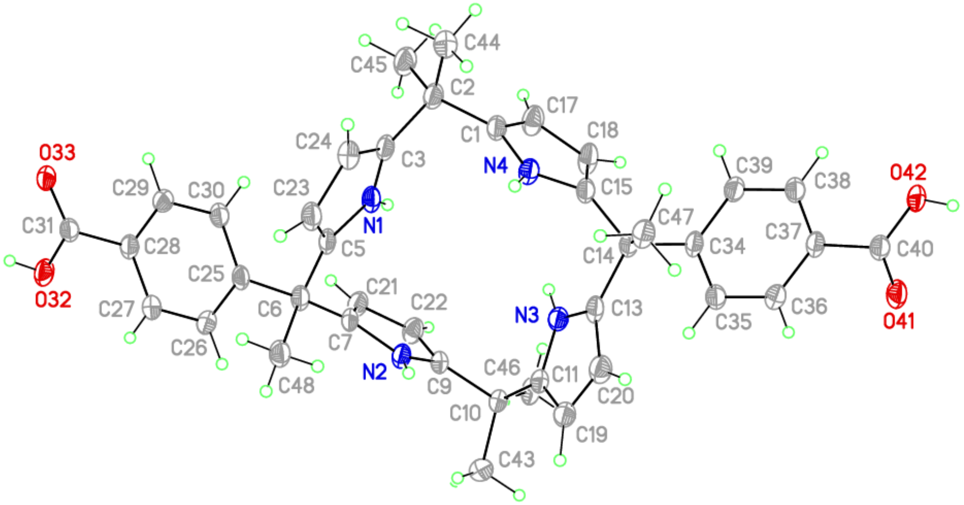

Figure S7. View of **1** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

X-ray Experimental for cage-2

Crystals grew as yellow prisms by slow evaporation from DMF and pyridine. The data crystal was cut from a larger crystal and had approximate dimensions; 0.32 x 0.18 x 0.15 mm. The data were collected at -140 °C on a Nonius Kappa CCD diffractometer using a Bruker AXS Apex II detector and a graphite monochromator with MoKα radiation (λ = 0.71073 Å). Reduced temperatures were maintained by use of an Oxford Cryosystems 600 low-temperature device. A total of 1013 frames of data were collected using φ and ω-scans with a scan range of 0.8° and a counting time of 73 seconds per frame. Details of crystal data, data collection and structure refinement are listed in Table S2. Data reduction were performed using SAINT V8.27B.[9] The structure was solved by direct methods using SHELXT[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2016/6.[3] Structure analysis was aided by use of the programs PLATON[4] and WinGX.[5]

A region of the unit cell had some badly disordered solvent. Attempts to model the disorder were unsatisfactory. The contributions to the scattering factors due to these solvent molecules were removed by use of the utility SQUEEZE[10] in PLATON.

The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0547*P)^2 + (39.9071*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.155, with R(F) equal to 0.0610 and a goodness of fit, S, = 1.06. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[6] The data were checked for secondary extinction but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[7] All figures were generated using SHELXTL/PC.[8] Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found in the CIF. CCDC deposition number: 1850739.

Table S2. Crystal data and structure refinement for **cage-2**.

Identification code	shelx	
Empirical formula	C192 H200 N24 O32 U4	
Formula weight	4307.87	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 19.2663(11) Å	α = 90°.
	b = 25.3809(14) Å	β = 96.389(3)°.
	c = 24.2879(13) Å	γ = 90°.
Volume	11802.9(11) $Å^3$	
Z	2	
Density (calculated)	1.212 Mg/m^3	
Absorption coefficient	2.797 mm^{-1}	
F(000)	4288	
Crystal size	0.317 x 0.181 x 0.154 mm^3	
Theta range for data collection	2.055 to 25.510°.	
Index ranges	-23<=h<=23, -29<=k<=30, -29<=l<=28	
Reflections collected	175332	
Independent reflections	21767 [R(int) = 0.1313]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Numerical	
Max. and min. transmission	1.00 and 0.691	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	21767 / 812 / 1141	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0610, wR2 = 0.1237	
R indices (all data)	R1 = 0.1414, wR2 = 0.1550	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.120 and -1.028 e. $Å^{-3}$	

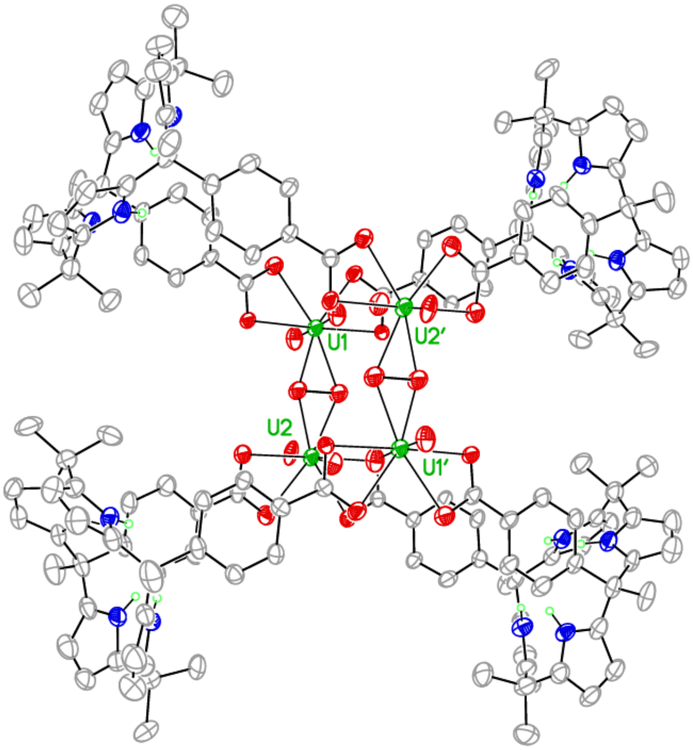

Figure S8. View of **cage-2** showing the U atom labeling scheme. Displacement ellipsoids are scaled to the 30% probability level. The complex resides around a crystallographic inversion center at ½, ½, ½. Atoms with labels appended by a ‘ are related by 1-x, 1-y, 1-z.

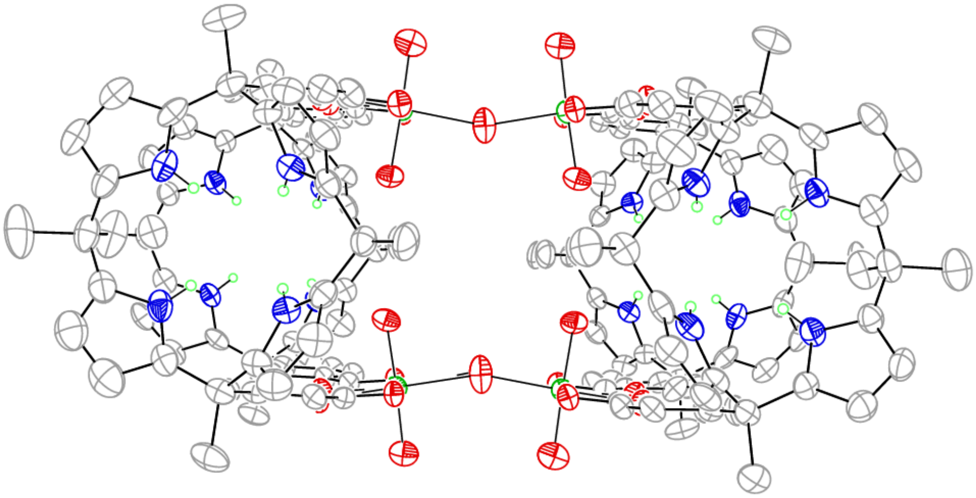

Figure S9. Side view of **cage-2**. Displacement ellipsoids are scaled to the 30% probability level.

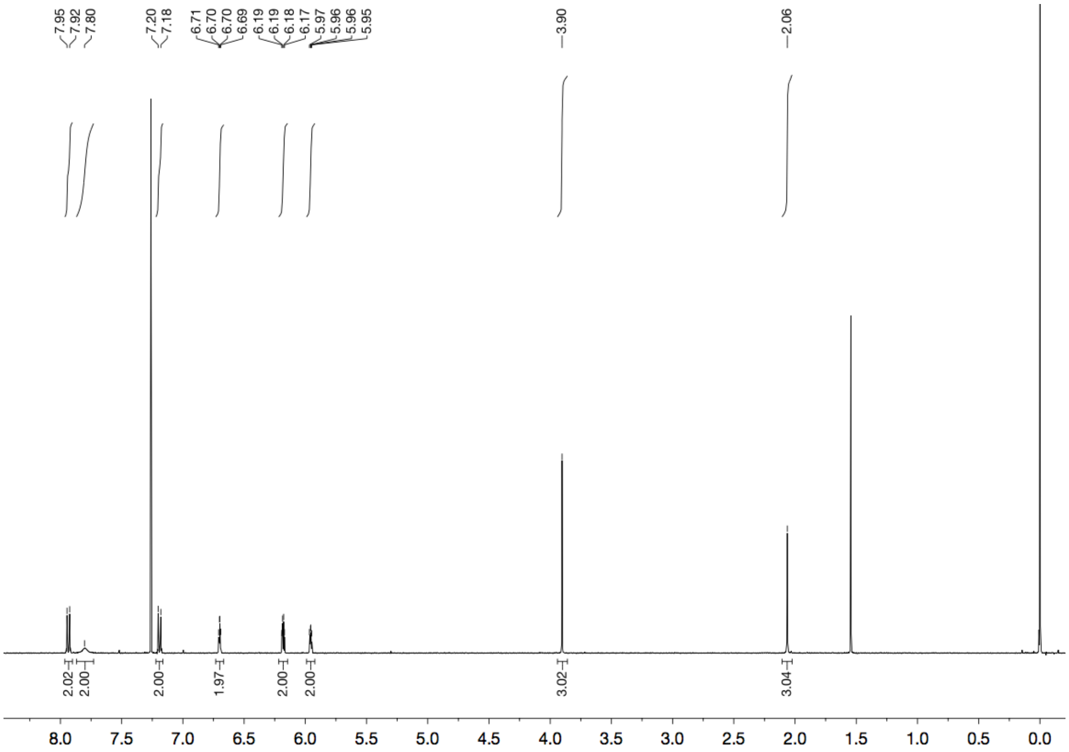

Figure S10. ^{1}H NMR spectrum of **3** recorded in $CDCl_3$.

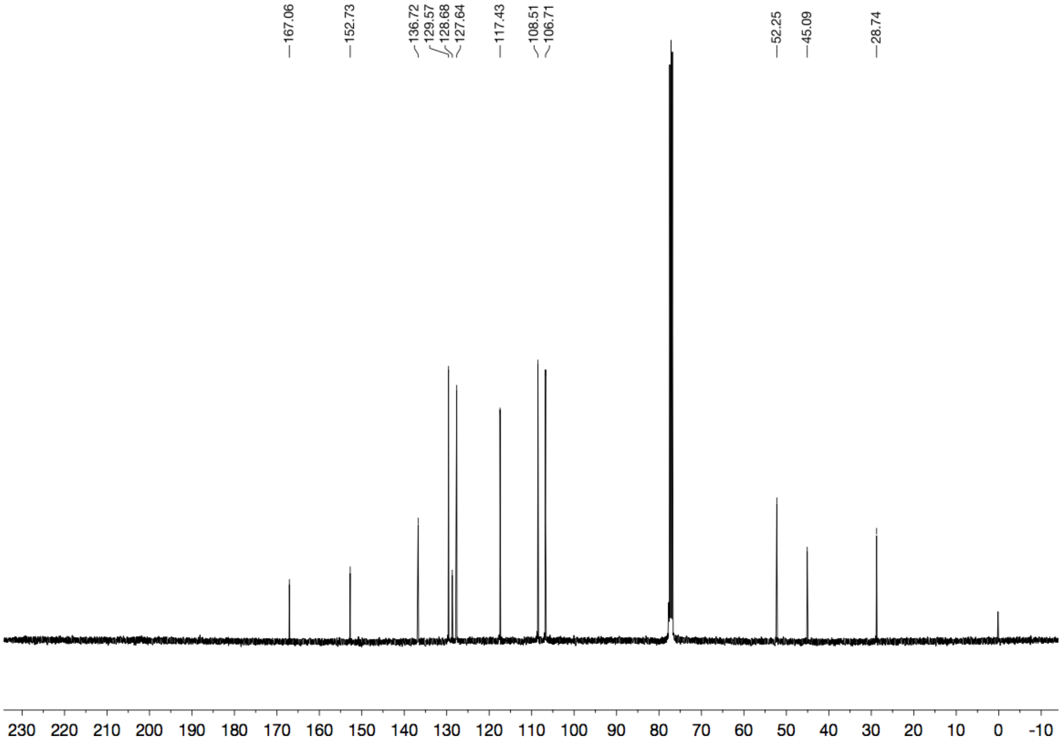

Figure S11. ^{13}C NMR spectrum of **3** recorded in $CDCl_3$.

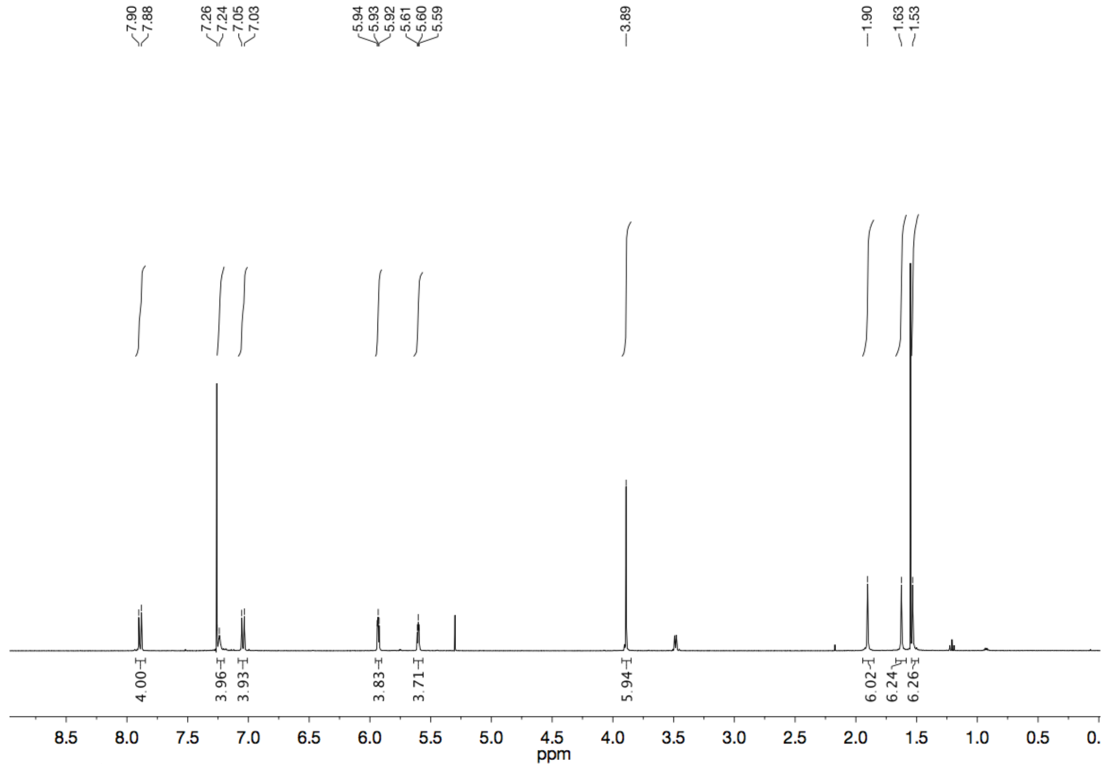

Figure S12. ^{1}H NMR spectrum of **4** recorded in CDCl$_3$.

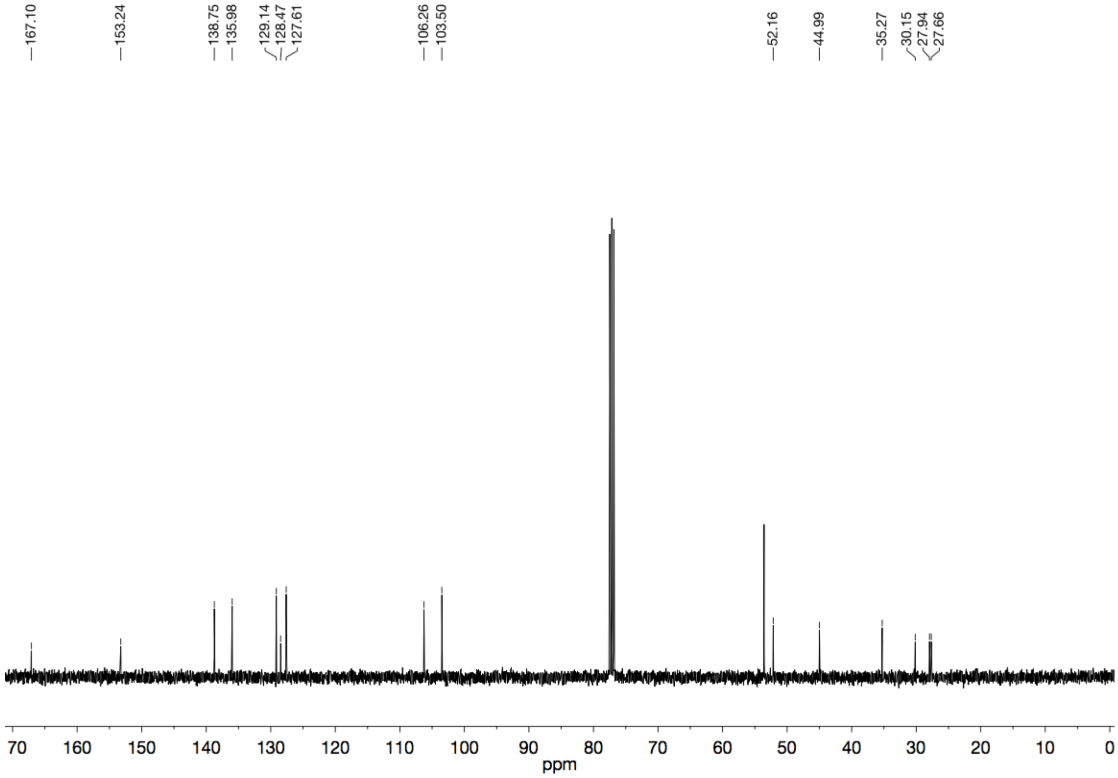

Figure S13. ^{13}C NMR spectrum of **4** recorded in CDCl$_3$.

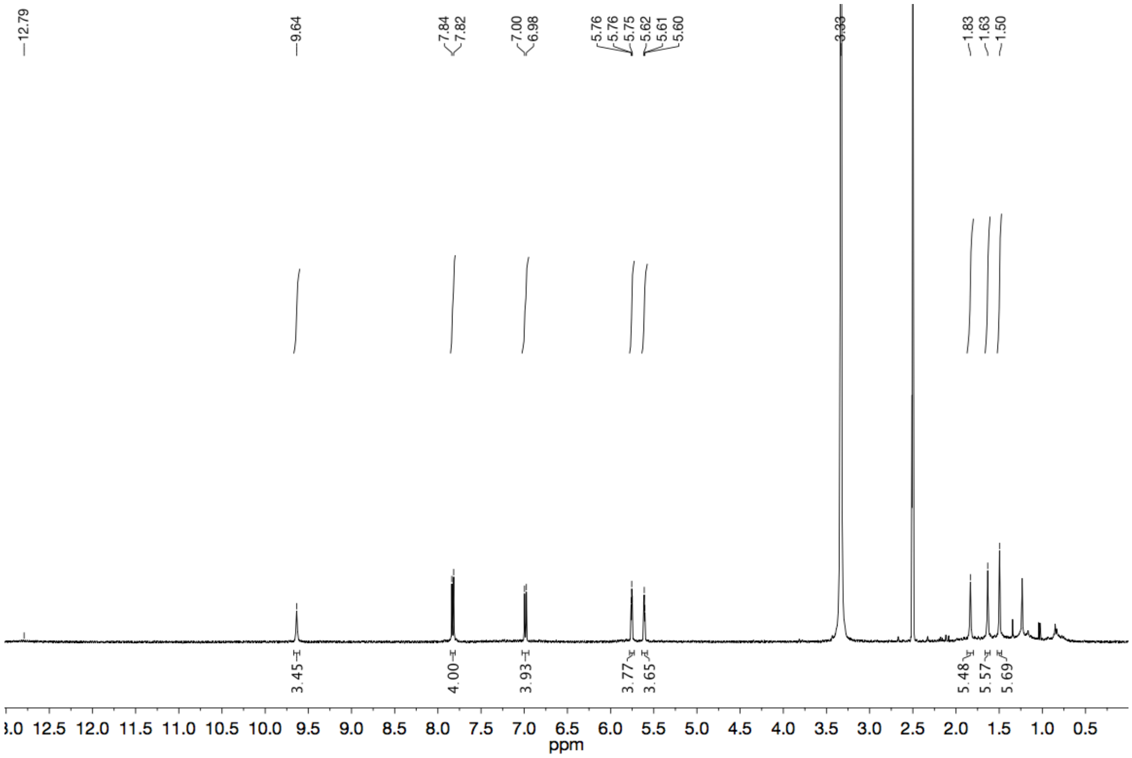

Figure S14. ^{1}H NMR spectrum of **1** recorded in DMSO-d_6.

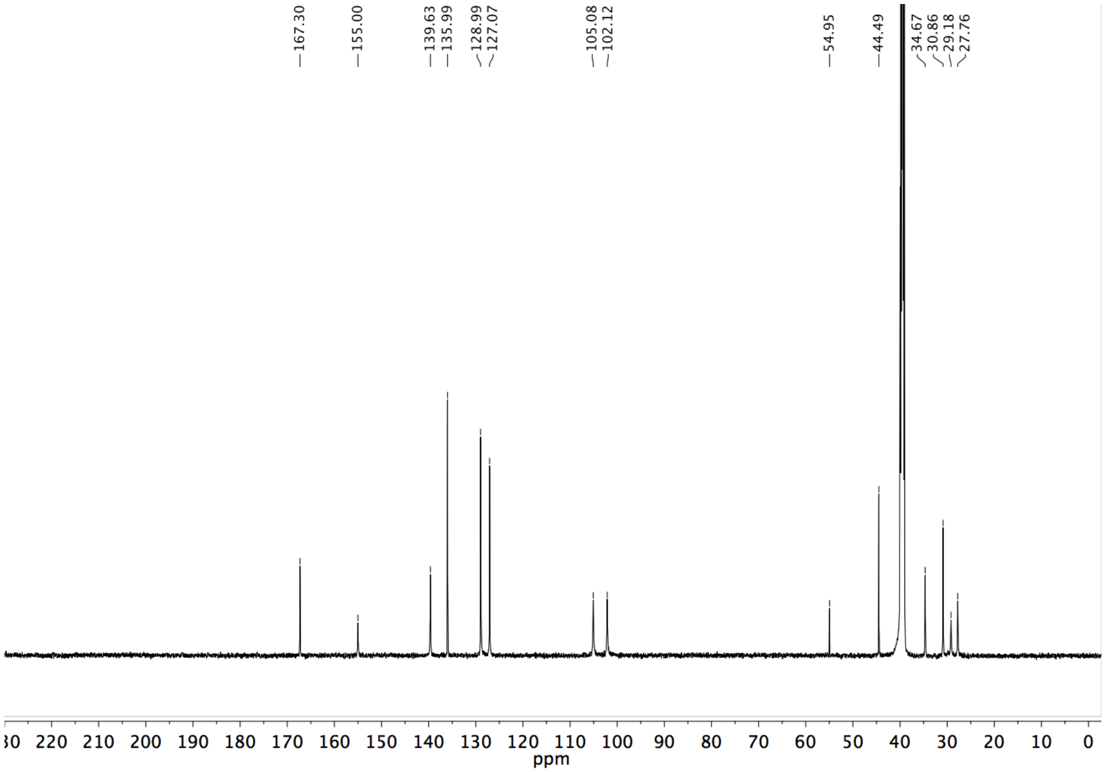

Figure S15. ^{13}C NMR spectrum of **1** recorded in DMSO-d_6.

References

1) CrysAlisPro. Agilent Technologies, Agilent Technologies UK Ltd., Oxford, UK, SuperNova CCD System, CrysAlicPro Software System, 1.171.39.46, 2013

2) G. M. Sheldrick, SHELXT (A program for the automatic solution of crystal structures), *Acta. Cryst.*, 2015, **A71**, 3-8.

3) G. M. Sheldrick, SHELXL-2016/6 (Program for the Refinement of Crystal Structures), *Acta Cryst.*, 2015, **C71**, 9-18.

4) A. L. Spek, PLATON (A Multipurpose Crystallographic Tool. Utrecht University, The Netherlands), *Acta Cryst.*, 2009, **D65**, 148-155.

5) L. J. Farrugia, WinGX 1.64 (An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single Crystal X-ray Diffraction Data), *J. Appl. Cryst.*, 1999, **32**. 837-838.

6) $R_w(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|)^4\}^{1/2}$ where w is the weight given each reflection.
$R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$.
$S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

7) International Tables for X-ray Crystallography, ed. A. J. C. Wilson, Kluwer Academic Press, Boston, 1992, Vol. C, Tables 4.2.6.8. and 6.1.1.4.

8) G. M. Sheldrick, SHELXTL/PC (Version 5.03). Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA, 1994.

9) SAINT V8.27B Bruker AXS Inc, Madison, WI, 2012.

10) P. V. D. Sluis and A. L. Spek, SQUEEZE, *Acta Cryst.*, 1990, **A46**, 194-201.