

Electronic Supplementary Information

**Co-crystals of tetrahaloauric acid and 1,3,5-(methylacetamide)benzene-based tectons:
consistent trapping of high energy molecular conformation**

Cassandra C. Shaffer, Allen G. Oliver, and Bradley D. Smith*
Department of Chemistry and Biochemistry,
University of Notre Dame,
Notre Dame, IN 46556, USA.
*Email: smith.115@nd.edu

Contents

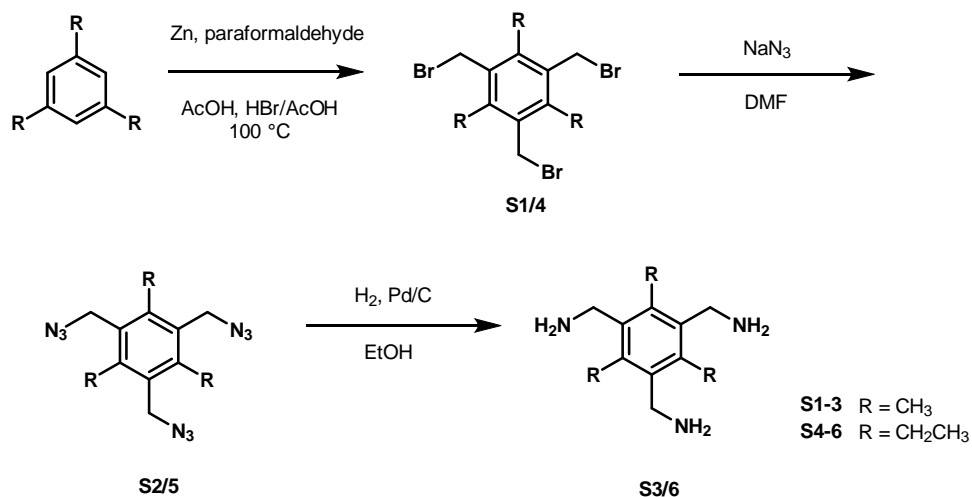
A. Synthesis.....	S2
B. Characterization Data.....	S3
C. Crystal Structure Data.....	S13
D. Hydrogen Bond Information.....	S22
E. Conformations.....	S23
F. References.....	S24

A. Synthesis

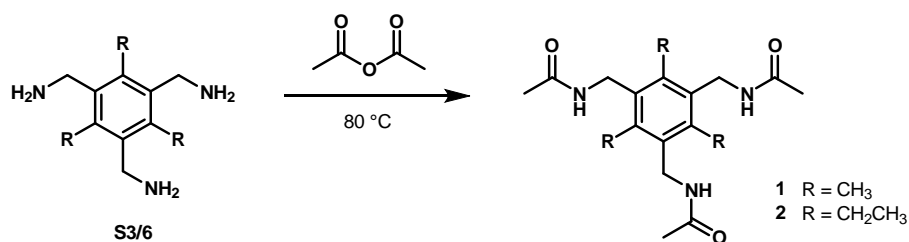
Compounds **S1** – **S6** were synthesized according to literature procedures.^{1,2}

Compound 1. Compound **S3** (0.32 g, 207.3 mmol) was suspended in acetic anhydride (10 mL) and stirred at 80 °C overnight. The solvent was removed under high vacuum to yield an off-white solid (0.40 g, 78%). ¹H-NMR (400 MHz, DMSO-d₆): δ 7.78 (t, 3H), 4.29 (d, J = 4.8 Hz, 6H), 2.28 (s, 9H), 1.81 (s, 9H) ppm. ¹³C-NMR (100 MHz, DMSO-d₆): δ 169.3, 136.6, 133.4, 38.5, 22.8, 16.2 ppm. HRMS (ESI): calculated for C₁₈H₂₈N₃O₃ [M+H]⁺ 334.2125, found 334.2121.

Compound 2. Prepared analogously to compound **1** starting from compound **S6**. Off-white solid, quantitative. ¹H-NMR (400 MHz, DMSO-d₆): δ 7.81 (t, 3H), 4.28 (d, J = 4.5 Hz, 6H), 2.66 (q, J = 7.3 Hz, 6H), 1.81 (s, 9H), 1.08 (t, J = 7.4 Hz, 9H) ppm. ¹³C-NMR (100 MHz, DMSO-d₆): δ 169.2, 143.5, 132.7, 37.4, 22.9, 22.8, 16.6 ppm. HRMS (ESI): calculated for C₂₁H₃₄N₃O₃ [M+H]⁺ 376.2595, found 376.2598.



Scheme S1. Summary of literature procedure followed to obtain **S1-S6**.



Scheme S2. Synthesis of tectons **1** and **2**.

B. Characterization Data

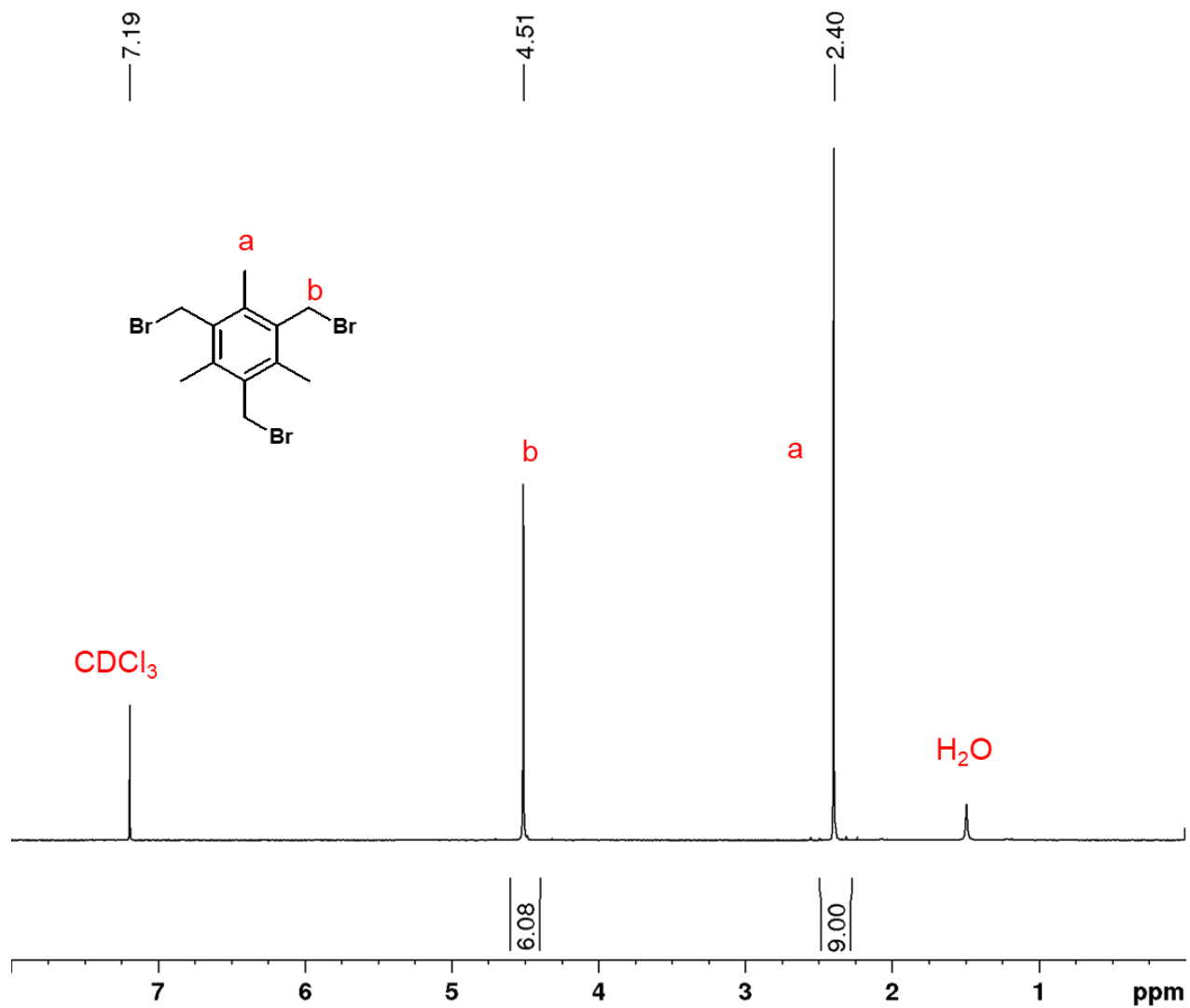


Figure S1. ¹H NMR (400 MHz, CDCl₃) of **S1**.

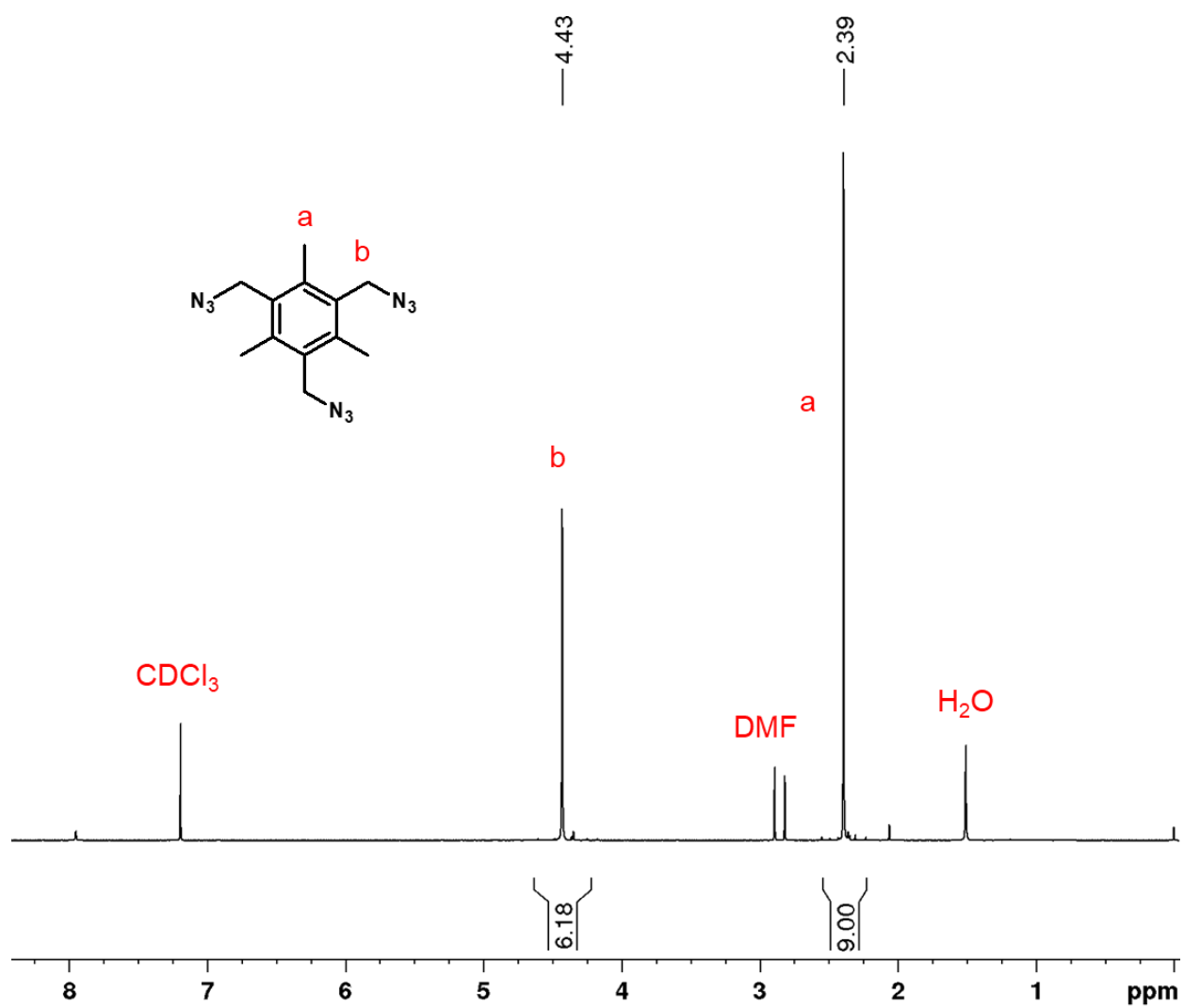


Figure S2. ¹H NMR (400 MHz, CDCl₃) of **S2**.

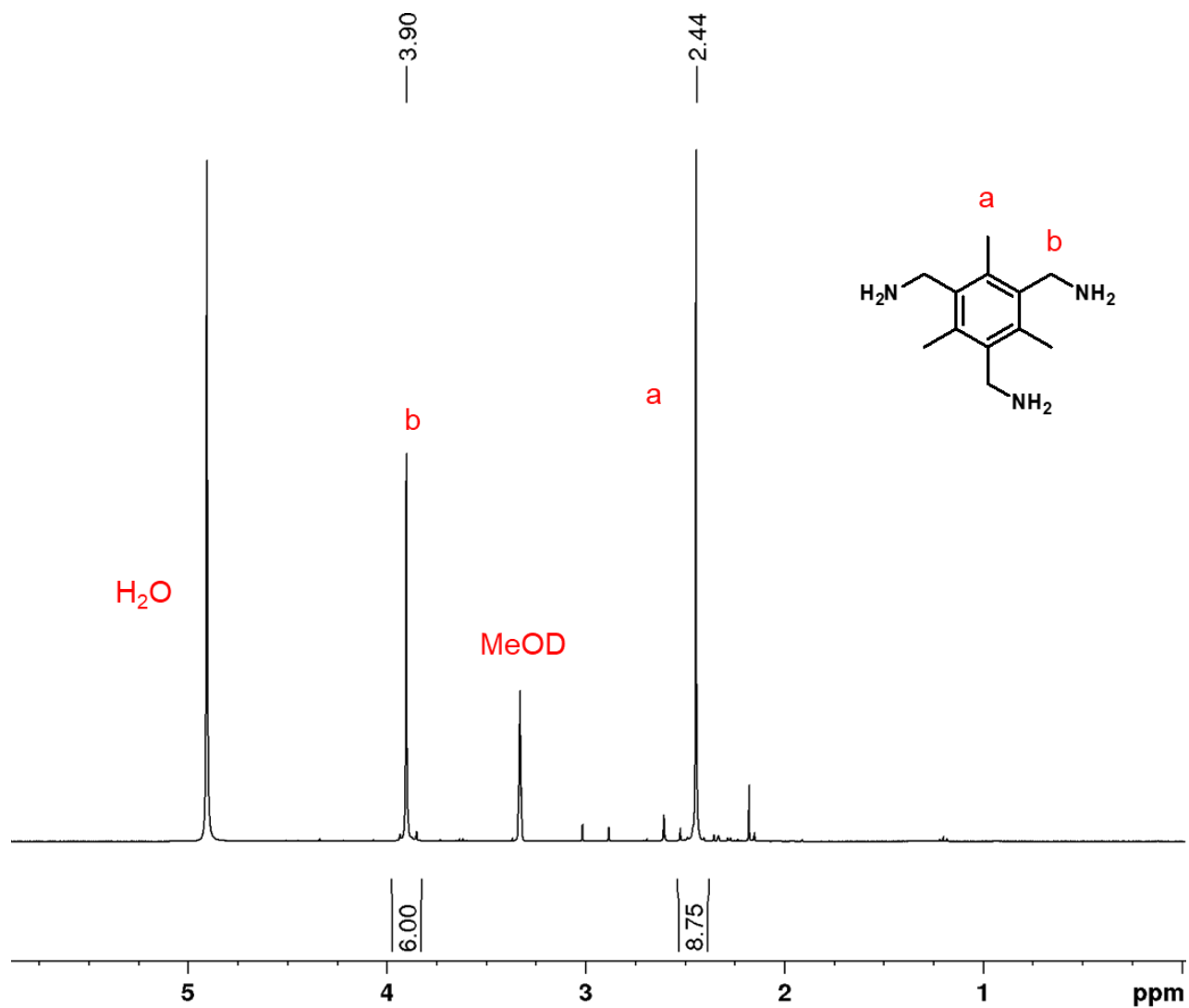


Figure S3. ^1H NMR (400 MHz, CD_3OD) of S3.

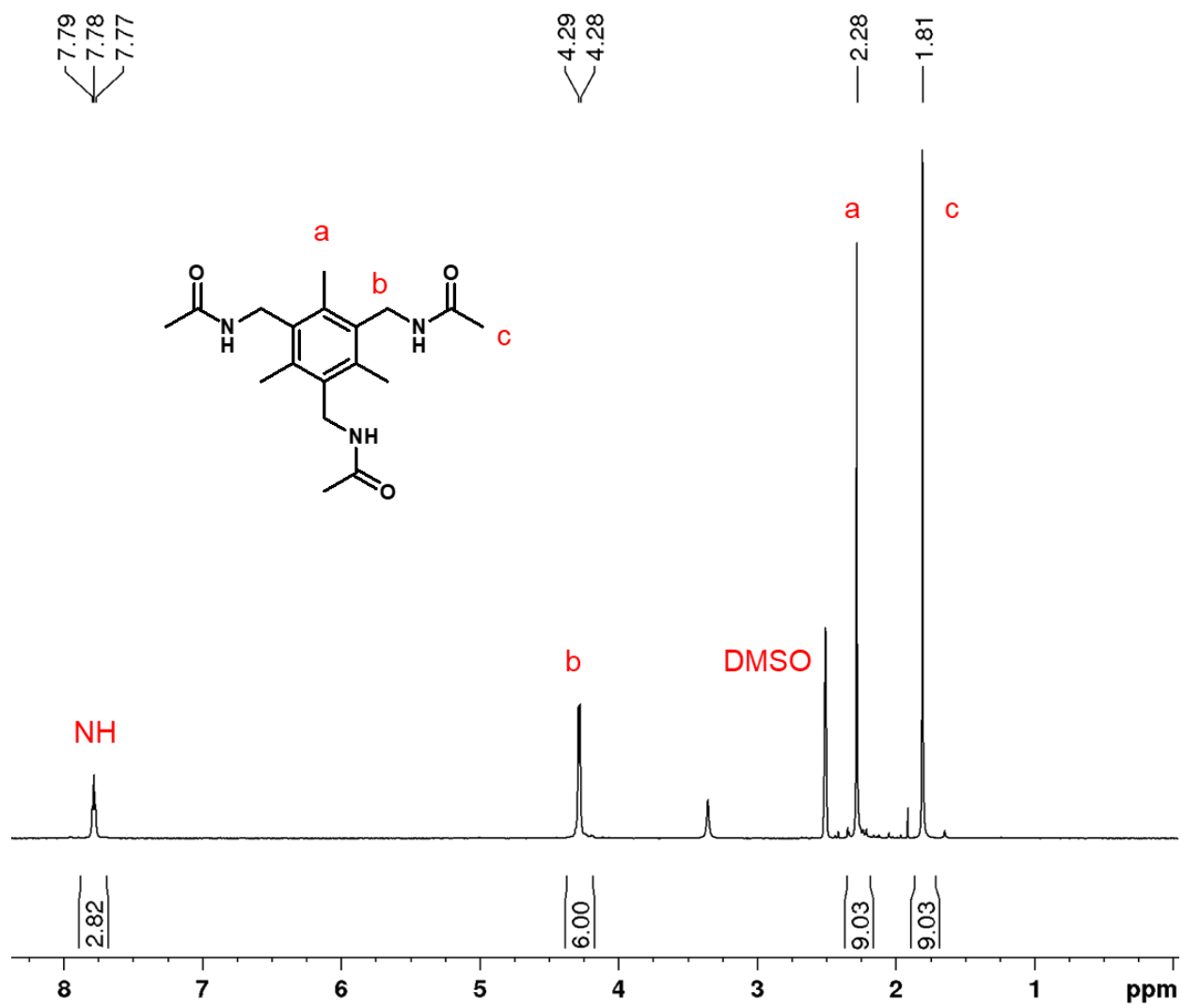


Figure S4. ¹H NMR (400 MHz, DMSO-d₆) of **1**.

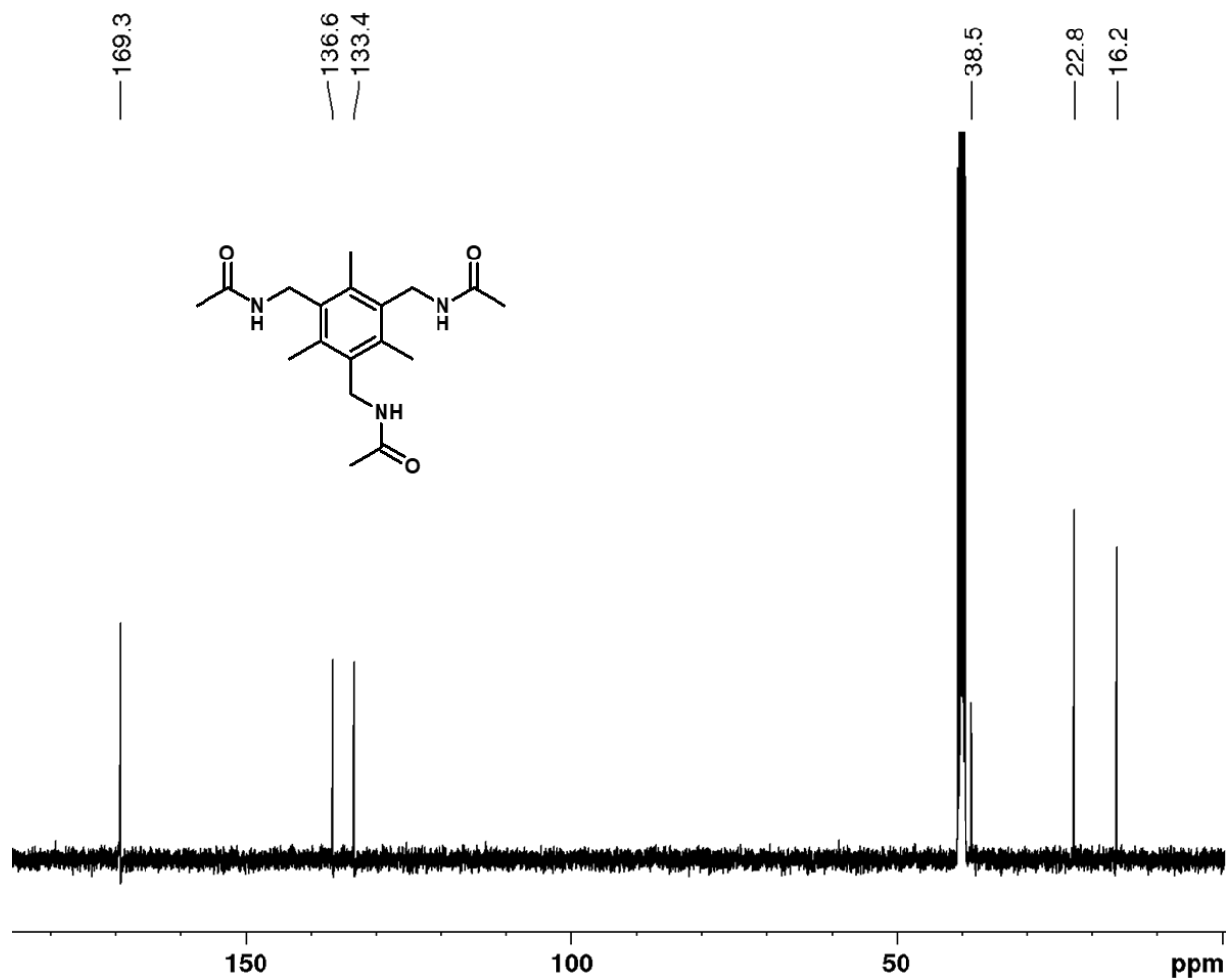


Figure S5. ^{13}C NMR (100 MHz, DMSO- d_6) of 1.

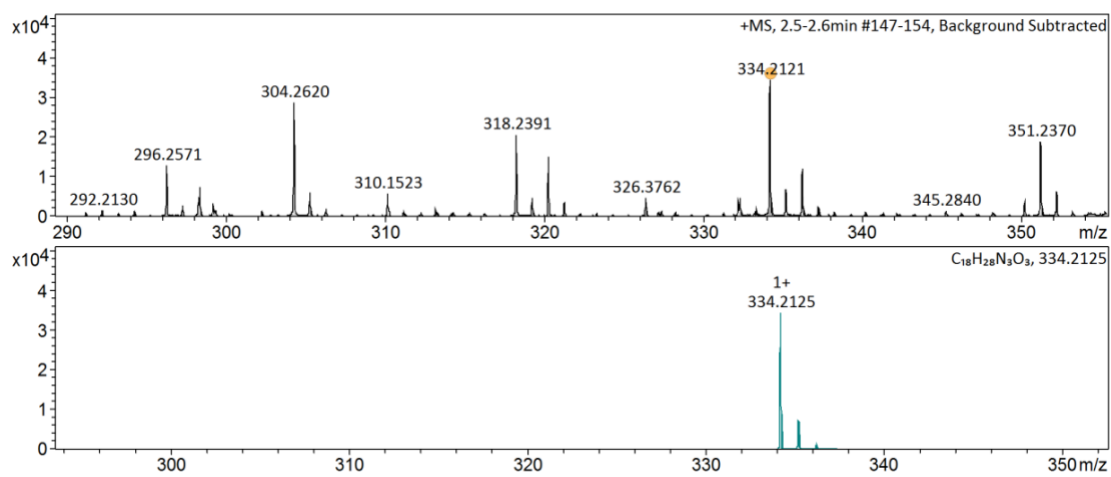


Figure S6. HRMS(ESI) of 1.

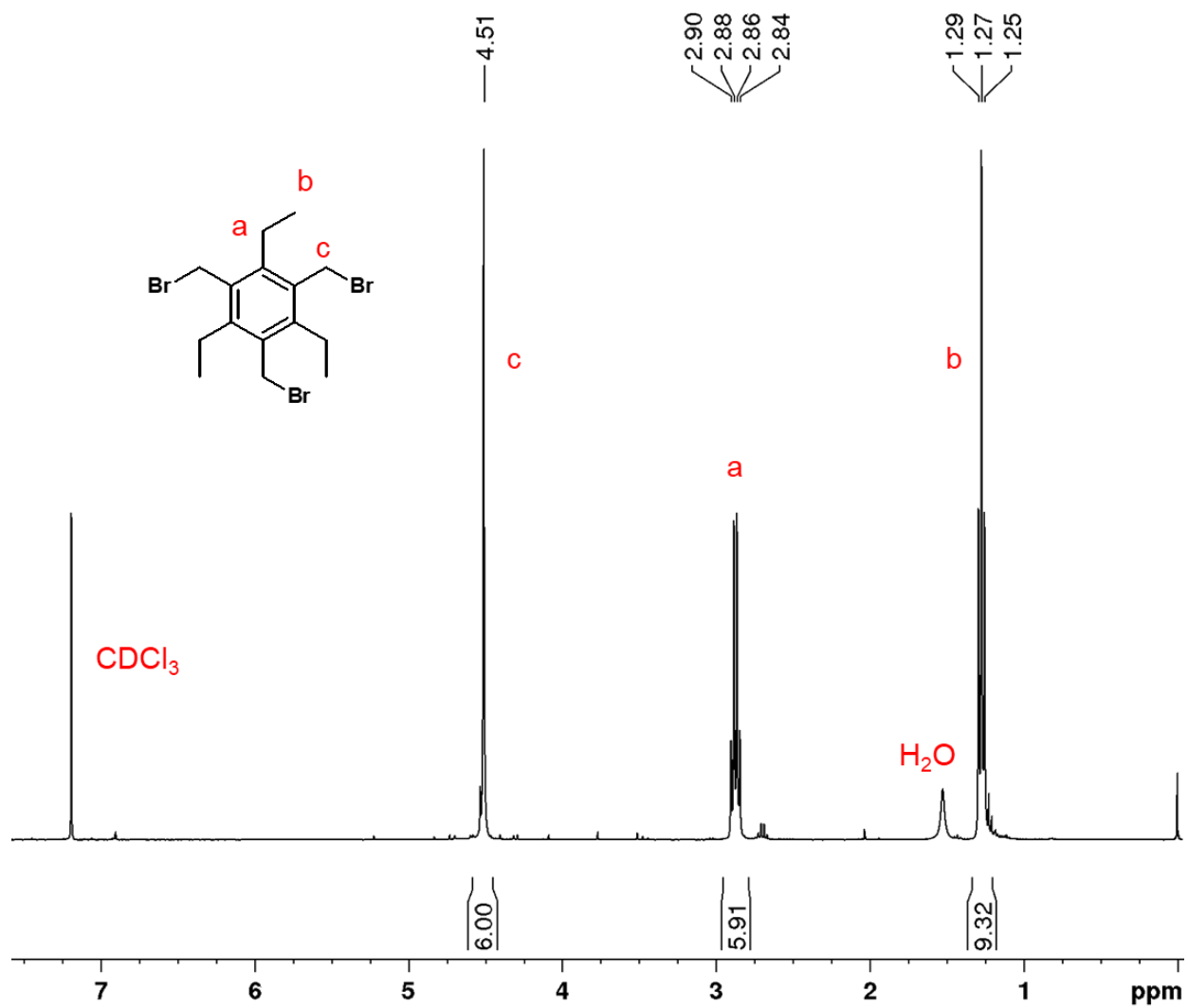


Figure S7. ¹H NMR (400 MHz, CDCl₃) of S4.

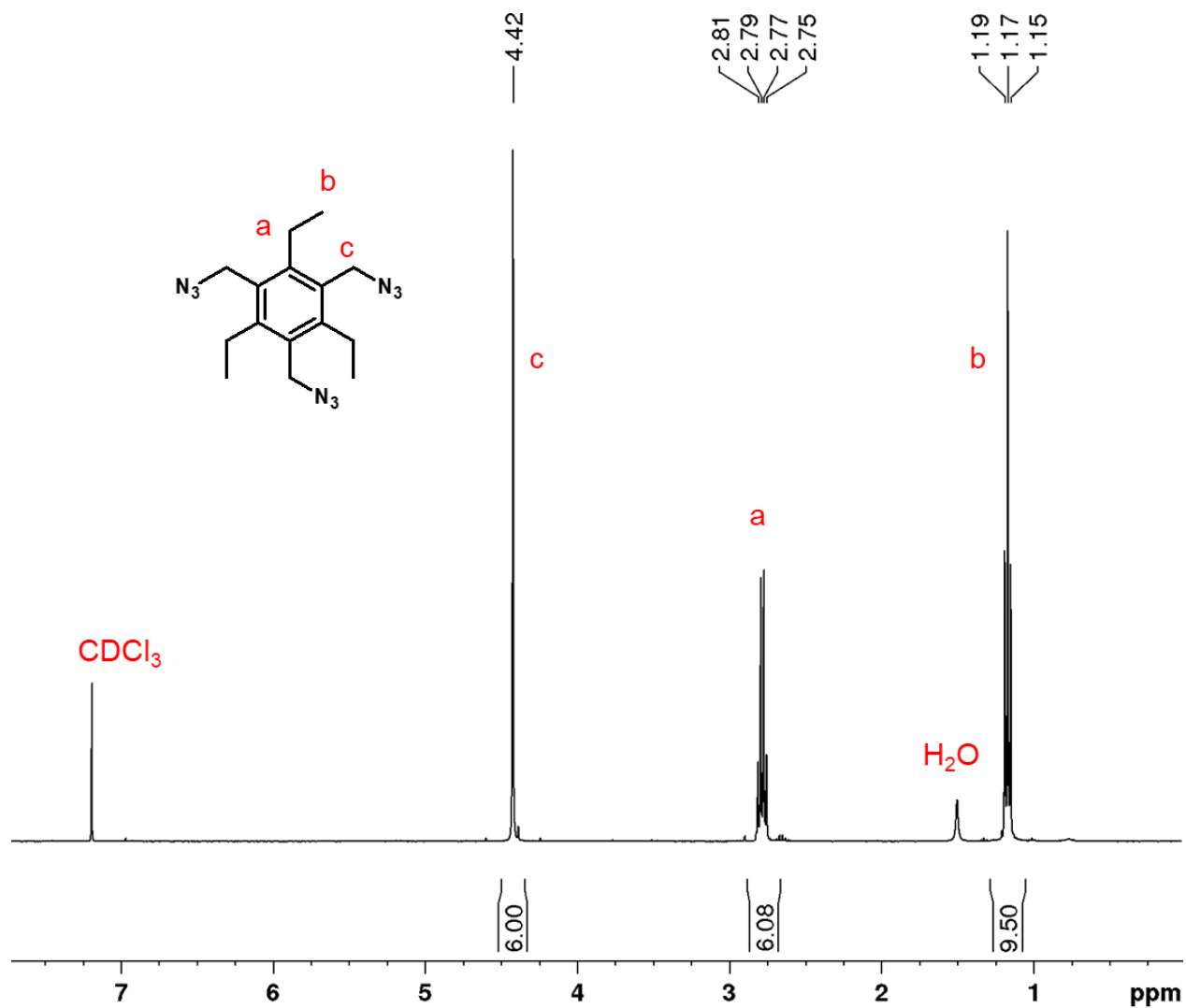


Figure S8. ¹H NMR (400 MHz, CDCl₃) of S5.

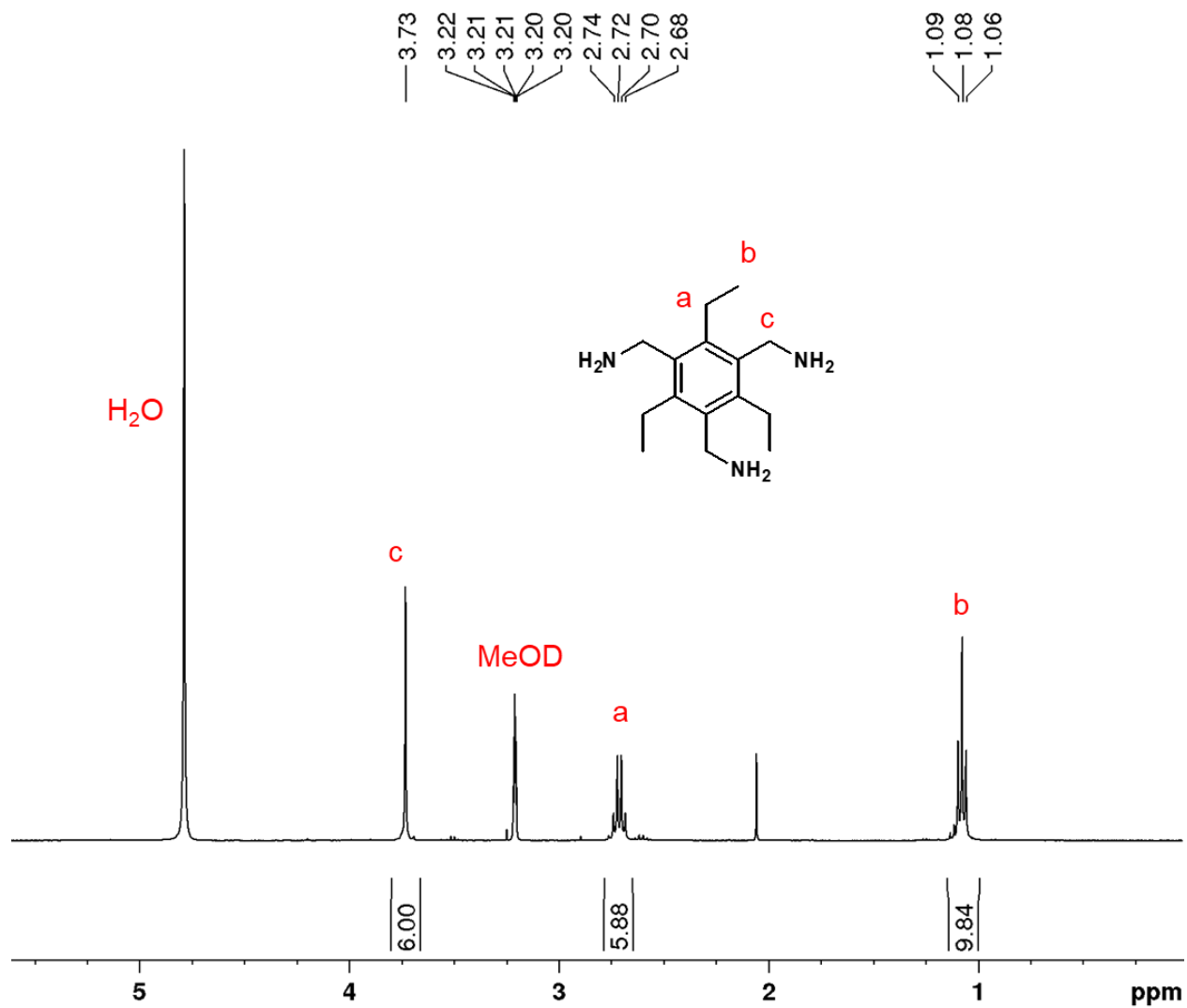


Figure S9. ¹H NMR (400 MHz, CD₃OD) of S6.

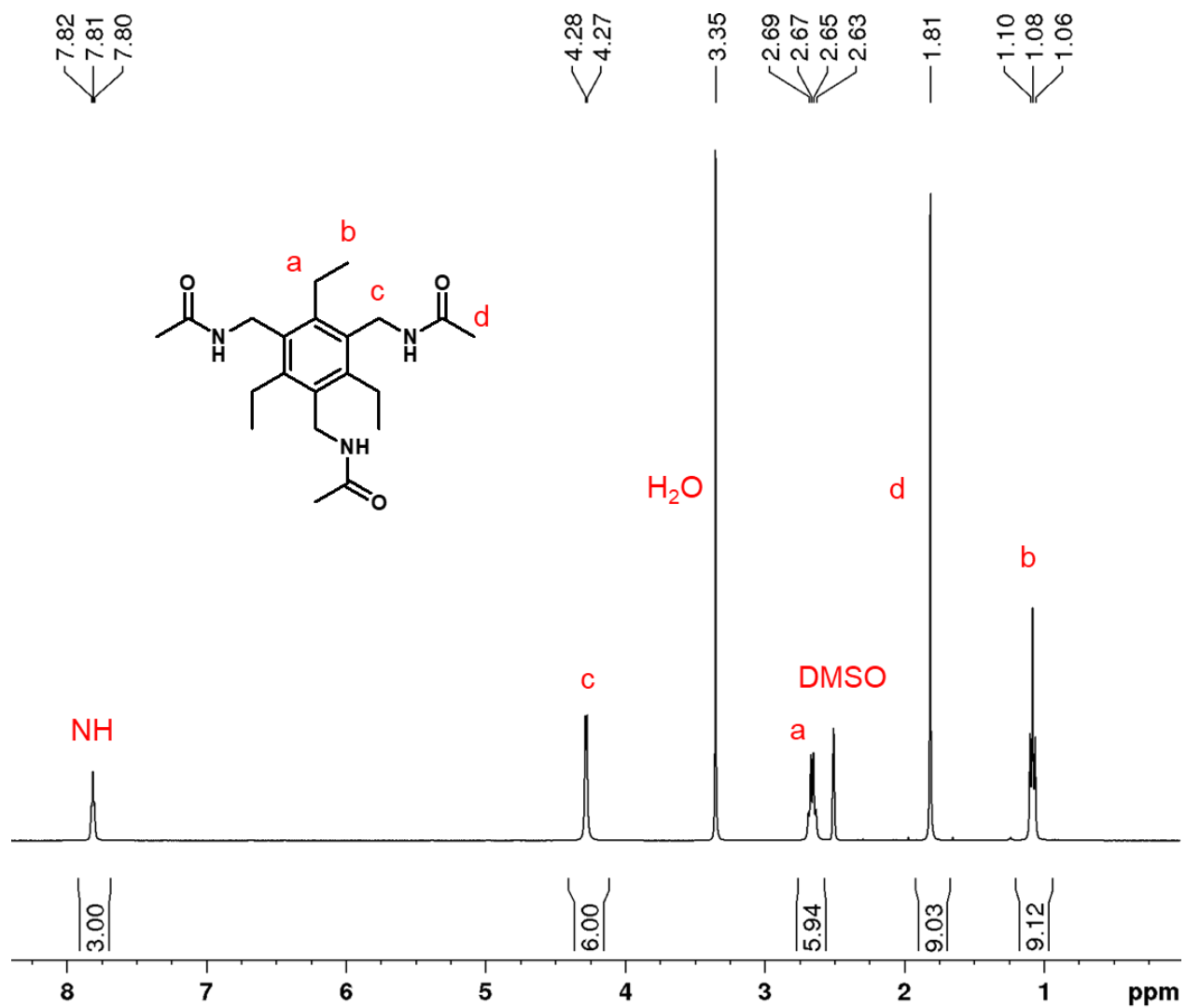


Figure S10. ^1H NMR (400 MHz, DMSO- d_6) of **2**.

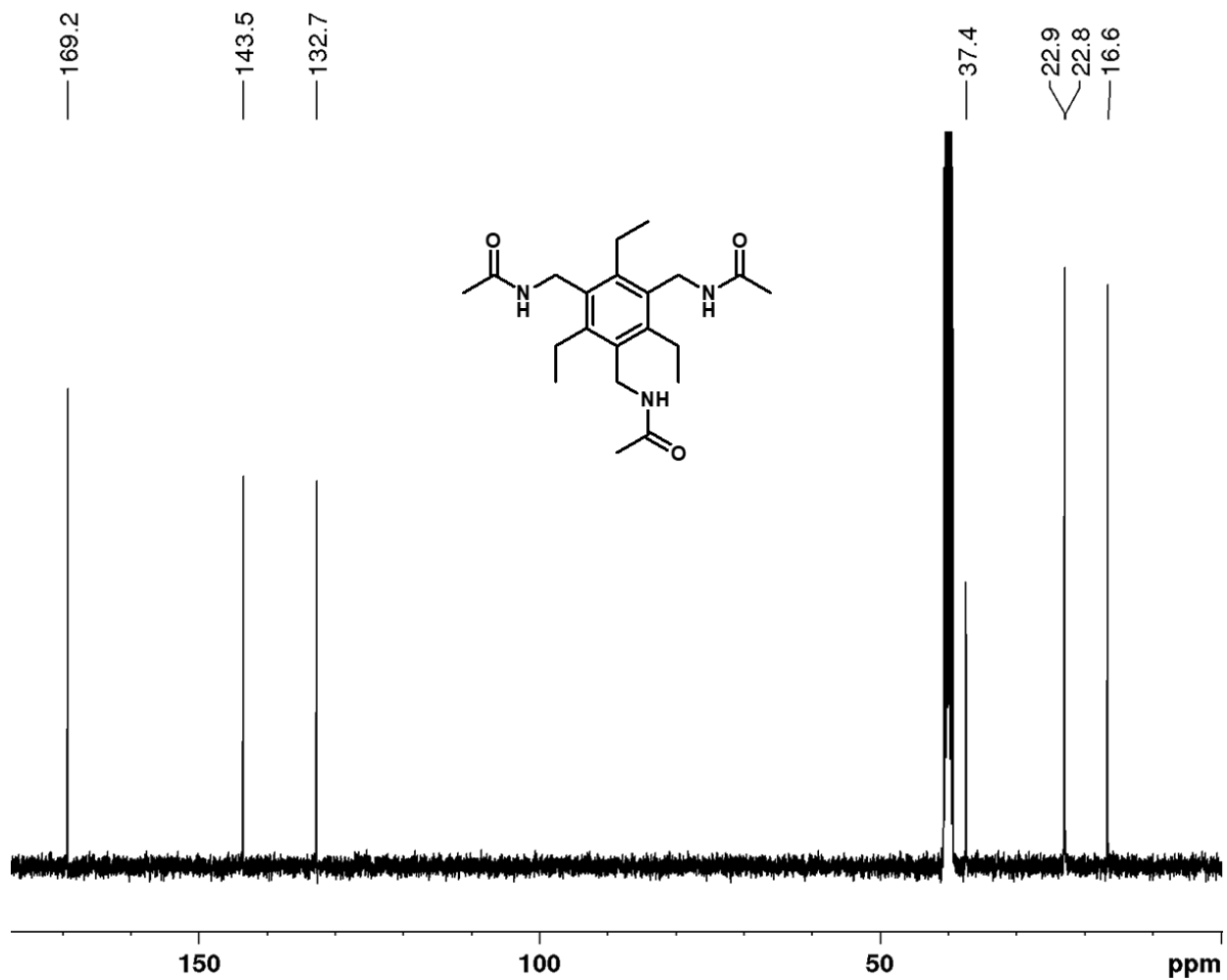


Figure S11. ¹³C NMR (100 MHz, DMSO-d₆) of **2**.

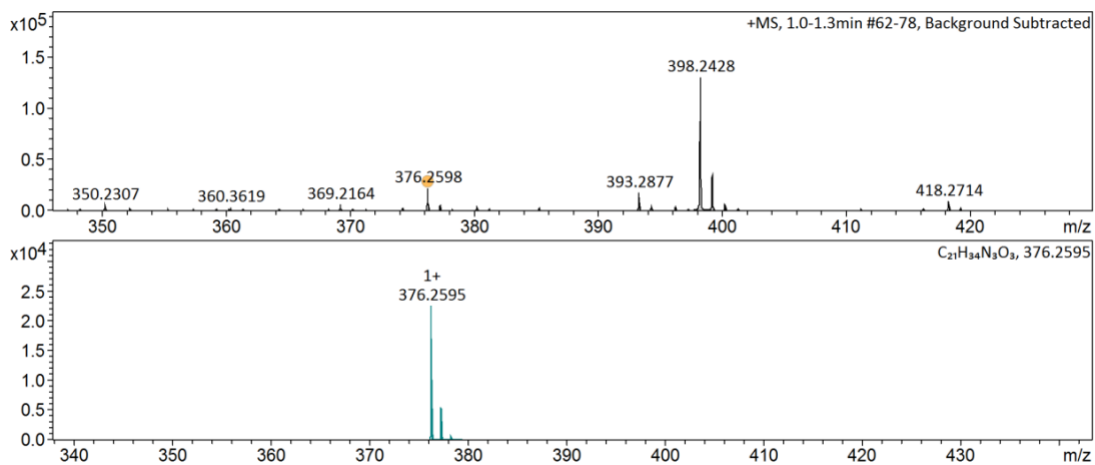


Figure S12. HRMS (ESI) of **2**.

C. Crystal Structure Data

1•HAuCl₄

The complex crystallizes as yellow block-like crystals from dichloromethane / methanol / diethyl ether solution. An arbitrary sphere of data was collected on a yellow block-like crystal, having approximate dimensions of $0.094 \times 0.035 \times 0.033$ mm, on a Bruker APEX-II diffractometer using a combination of ω - and ϕ -scans of 0.5° [3]. Data were corrected for absorption and polarization effects and analyzed for space group determination [4]. The structure was solved by dual-space methods and expanded routinely [5]. The model was refined by full-matrix least-squares analysis of F^2 against all reflections [6]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Atomic displacement parameters for the hydrogens were tied to the equivalent isotropic displacement parameter of the atom to which they are bonded ($U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl, $1.2U_{\text{eq}}(\text{C})$ for all others).

There are two molecules of the cation and anion in the unit cell of the primitive, centrosymmetric, triclinic space group P-1. The structure of the complex is as expected (see Figures). The tetrachloroaurate anion is located over the benzene ring and forms hydrogen bonds to two of the amide nitrogen atoms. The remaining amide nitrogen forms a hydrogen bond to a chlorine on a neighboring, symmetry-related tetrachloroaurate anion. The charge is balanced by the presence of a proton bonded to amide carbonyl oxygen O2, similar to previous examples. This forms a hydrogen bond to carbonyl oxygen O3 of a neighboring molecule.

Bond distances and angles within the molecules are unexceptional.

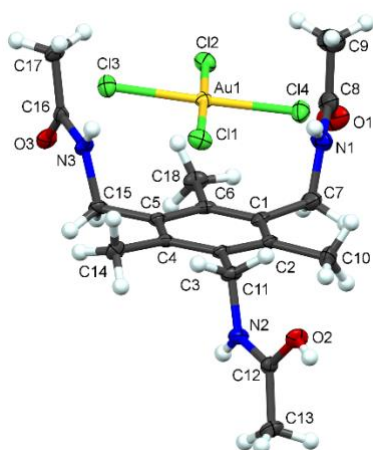


Figure S13. Atomic displacement plot and labeling scheme for **1**•HAuCl₄. Displacement parameters depicted at 50% probability and hydrogen atoms shown at an arbitrary radius.

Crystal data and structure refinement for **1**•HAuCl₄.

Identification code	nd1852	
Empirical formula	C ₁₈ H ₂₈ AuCl ₄ N ₃ O ₃	
Formula weight	673.20	
Temperature	120(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	$a = 7.0697(5)$ Å	$\alpha = 87.564(2)^\circ$
	$b = 12.8591(8)$ Å	$\beta = 80.1017(19)^\circ$
	$c = 13.3357(9)$ Å	$\gamma = 88.5666(19)^\circ$
Volume	1193.03(14) Å ³	
Z	2	
Density (calculated)	1.874 g.cm ⁻³	
Absorption coefficient (μ)	6.637 mm ⁻¹	
F(000)	656	
Crystal color, habit	yellow, block	
Crystal size	0.094 × 0.035 × 0.033 mm ³	
θ range for data collection	1.551 to 30.560°	
Index ranges	-10 ≤ h ≤ 10, -18 ≤ k ≤ 18, -19 ≤ l ≤ 19	
Reflections collected	34220	
Independent reflections	7286 [$R_{\text{int}} = 0.0532$]	
Completeness to $\theta = 25.242^\circ$	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.8721 and 0.6873	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	7286 / 0 / 284	
Goodness-of-fit on F ²	1.020	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0320$, $wR_2 = 0.0525$	
R indices (all data)	$R_1 = 0.0488$, $wR_2 = 0.0561$	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.714 and -1.493 e ⁻ .Å ⁻³	

1•HAuBr₄

The complex crystallizes as red blade-like crystals from dichloromethane / methanol / diethyl ether solution. An arbitrary sphere of data was collected on a red blade-like crystal, having approximate dimensions of $0.137 \times 0.093 \times 0.016$ mm, on a Bruker PHOTON-II diffractometer using a combination of ω - and ϕ -scans of 0.5° [3]. Data were corrected for absorption and polarization effects and analyzed for space group determination [4]. The structure was solved by dual-space methods and expanded routinely [5]. The model was refined by full-matrix least-squares analysis of F^2 against all reflections [6]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Atomic displacement parameters for the hydrogens were tied to the equivalent isotropic displacement parameter of the atom to which they are bonded ($U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl, $1.2U_{\text{eq}}(\text{C})$ for all others).

Data resolution on this complex was lower than typical, due to solvent and anion disorder within the structure. However, the connectivity is unequivocal and shows the expected compounds. Coupled with other structures this is a publishable structure, as long as derived metrics (bond distances and angles) are not the focus of the discussion.

The asymmetric unit consists of two cation/anion pairs and a half diethyl ether of crystallization (see Figures). The SQUEEZE routine from PLATON [7] was applied to diffuse residual electron density in the lattice. Initially a model emulating additional diethyl ether was attempted, but this yielded a very poor model. A total of 67 electrons of intensity in a void volume of 208 \AA^3 was recovered.

There are four molecules of the benzene cation and tetrabromoaurate anion and one modeled diethyl ether in the unit cell of the primitive, centrosymmetric, triclinic space group P-1.

The charge balancing hydrogen atoms were located on two amide oxygen atoms that had close approaches to amide oxygen atoms on neighboring molecules (see Table of Hydrogen Bonds). These hydrogen atoms could not be observed in a Fourier difference map and were modeled solely on location.

The packing of the molecules is such that the two independent benzene moieties π -stack with each other and one tetrabromoaurate intercalates with these pairs. The second tetrabromoaurate is oriented almost perpendicular to the planes of the other three main molecules.

One amide nitrogen, N6 is not involved in hydrogen bonding within the structure. This atom is oriented towards the void space, where, presumably, it would form a hydrogen bond with a solvent molecule. All other amide nitrogen atoms are involved in intermolecular hydrogen bonding interactions with anions and neighboring benzene moieties.

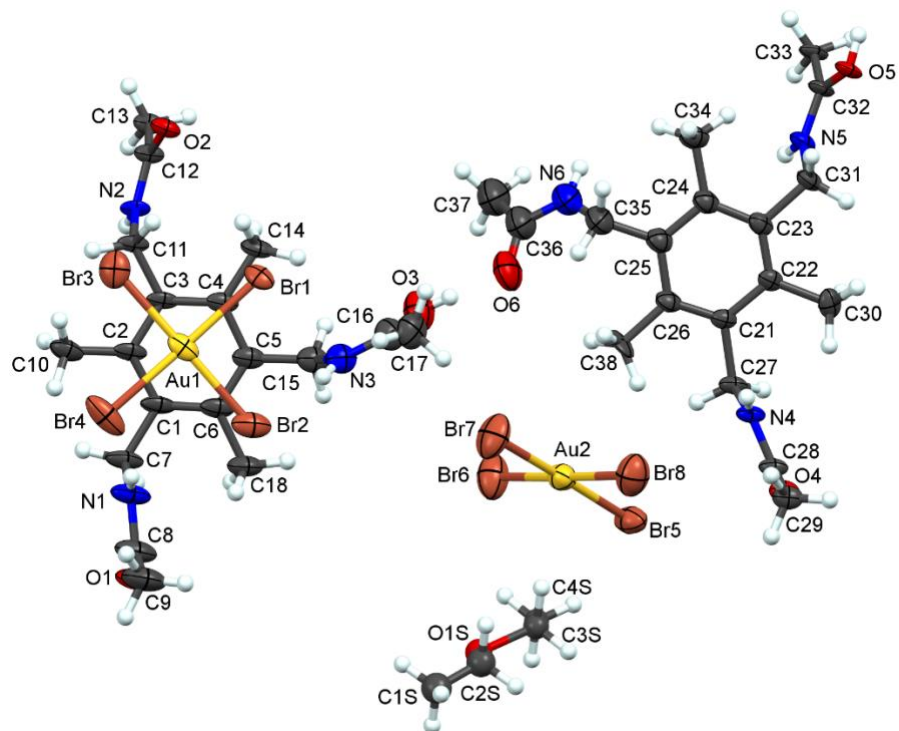


Figure S14. Labeling scheme for **1**·HAuBr₄. Atomic displacement ellipsoids depicted at 50% probability and hydrogen atoms shown as spheres of an arbitrary radius.

Crystal data and structure refinement for **1**•HAuBr₄.

Identification code	nd1854_sq
Empirical formula	C ₇₆ H ₁₂₂ Au ₄ Br ₁₆ N ₁₂ O ₁₃
Formula weight	3478.27
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	$a = 11.433(3)$ Å $\alpha = 71.990(5)^\circ$ $b = 14.321(4)$ Å $\beta = 82.849(5)^\circ$ $c = 19.606(6)$ Å $\gamma = 74.244(4)^\circ$
Volume	2935.2(15) Å ³
Z	1
Density (calculated)	1.968 g.cm ⁻³
Absorption coefficient (μ)	10.480 mm ⁻¹
F(000)	1642
Crystal color, habit	red, blade
Crystal size	0.137 × 0.093 × 0.016 mm ³
θ range for data collection	1.093 to 23.256°
Index ranges	-12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -21 ≤ l ≤ 21
Reflections collected	29675
Independent reflections	8423 [R _{int} = 0.0973]
Completeness to $\theta = 23.256^\circ$	100.0 %
Absorption correction	Numerical
Max. and min. transmission	0.8718 and 0.4190
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8423 / 292 / 555
Goodness-of-fit on F ²	0.977
Final R indices [I > 2 σ (I)]	R ₁ = 0.0837, wR ₂ = 0.2106
R indices (all data)	R ₁ = 0.1279, wR ₂ = 0.2383
Extinction coefficient	n/a
Largest diff. peak and hole	5.955 and -3.123 e ⁻ .Å ⁻³

2•HAuCl₄

The complex crystallizes as yellow block-like crystals from dichloromethane / methanol / diethyl ether solution. An arbitrary sphere of data was collected on a yellow block-like crystal, having approximate dimensions of $0.236 \times 0.212 \times 0.123$ mm, on a Bruker Kappa X8-APEX-II diffractometer using a combination of ω - and ϕ -scans of 0.5° [3]. Data were corrected for absorption and polarization effects and analyzed for space group determination [4]. The structure was solved by dual methods and expanded routinely [5]. The model was refined by full-matrix least-squares analysis of F^2 against all reflections [6]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Atomic displacement parameters for the hydrogens were tied to the equivalent isotropic displacement parameter of the atom to which they are bonded ($U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl, $1.2U_{\text{eq}}(\text{C})$ for all others).

There are four molecules of the complex in the unit cell of the primitive, centrosymmetric, monoclinic space group $P2_1/n$.

There are two independent, half gold tetrachloride anions in the asymmetric unit. Each is located on an inversion center (0.5, 0.5, 0 and 0.5, 0.5, 0.5). There is one complete 1,3,5-triacetamido-2,4,6-triethylbenzene within the asymmetric unit (see Figures). Au2 is located between pairs of benzene rings with Cl4 hydrogen bonded by N2 and N3 of the two neighboring amides. In contrast, Au1 gold tetrachloride is oriented almost perpendicular to the plane of the benzene ring. The chlorine atoms on this anion are not involved in hydrogen bonding. The amide hydrogen atoms and charge balancing hydrogen located between O1 and O3ⁱ (symmetry code (i): $-x+1, -y+1, -z$) were all located from a difference Fourier map. The remaining amide nitrogen, N1, forms a hydrogen bond to the carbonyl oxygen, O2, of an adjacent amide.

No unusual bond distances or angles were observed within the molecules.

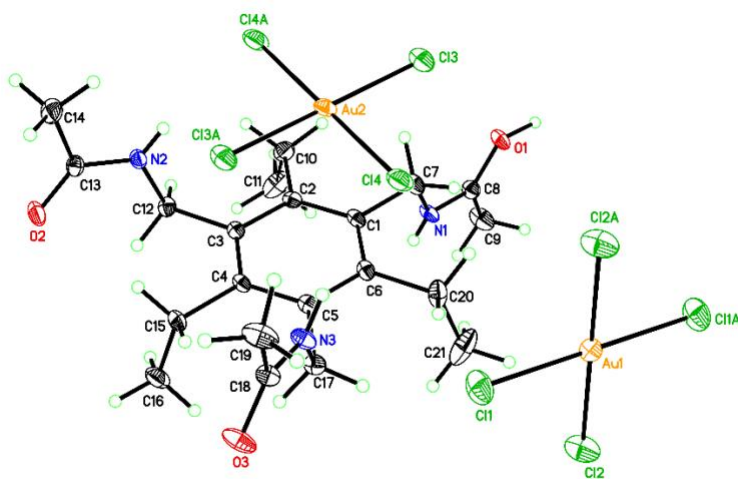


Figure S15. Labeling scheme and atomic displacement plot for **2•HAuCl₄**. Atomic displacement ellipsoids depicted at 50% probability and hydrogen atoms shown as spheres of an arbitrary radius.

Crystal data and structure refinement for 2•HAuCl₄.

Identification code	nd1903
Empirical formula	C ₂₁ H ₃₄ AuCl ₄ N ₃ O ₃
Formula weight	715.28
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /n
Unit cell dimensions	$a = 12.3290(9) \text{ \AA}$ $\alpha = 90^\circ$ $b = 16.7583(13) \text{ \AA}$ $\beta = 102.9930(10)^\circ$ $c = 13.2907(10) \text{ \AA}$ $\gamma = 90^\circ$
Volume	2675.7(3) Å ³
Z	4
Density (calculated)	1.776 g.cm ⁻³
Absorption coefficient (μ)	5.925 mm ⁻¹
F(000)	1408
Crystal color, habit	yellow, block
Crystal size	0.236 × 0.212 × 0.123 mm ³
θ range for data collection	1.987 to 30.465°
Index ranges	-17 ≤ h ≤ 17, -23 ≤ k ≤ 23, -18 ≤ l ≤ 18
Reflections collected	55484
Independent reflections	8132 [R _{int} = 0.0193]
Completeness to θ = 25.242°	100.0 %
Absorption correction	Numerical
Max. and min. transmission	0.4968 and 0.1901
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8132 / 0 / 314
Goodness-of-fit on F ²	1.075
Final R indices [I > 2σ(I)]	R ₁ = 0.0167, wR ₂ = 0.0346
R indices (all data)	R ₁ = 0.0269, wR ₂ = 0.0380
Extinction coefficient	n/a
Largest diff. peak and hole	0.475 and -0.773 e ⁻ .Å ⁻³

2•HAuBr₄

The complex crystallizes as orange block-like crystals from dichloromethane / methanol / diethyl ether solution. An arbitrary sphere of data was collected on an orange block-like crystal, having approximate dimensions of $0.189 \times 0.149 \times 0.088$ mm, on a Bruker APEX-II diffractometer using a combination of ω - and ϕ -scans of 0.5° [3]. Data were corrected for absorption and polarization effects and analyzed for space group determination [4]. The structure was solved by dual-space methods and expanded routinely [5]. The model was refined by full-matrix least-squares analysis of F^2 against all reflections [6]. All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Atomic displacement parameters for the hydrogens were tied to the equivalent isotropic displacement parameter of the atom to which they are bonded ($U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl, $1.2U_{\text{eq}}(\text{C})$ for all others).

There are four molecules of the complex in the unit cell of the primitive, centrosymmetric monoclinic space group $P2_1/n$.

The structure is isomorphous with the tetrachloroaurate homologue (**2**•HAuCl₄). The naming convention adopted in that structure is used here. The asymmetric unit consists of two half tetrabromoaurate anions, each is located on independent inversion centers (0.5, 0.5, 0 and 0.5, 0.5, 0.5).

The amide and charge-balancing hydrogen atoms were all located from a difference Fourier map. The amide nitrogen, N1, forms a hydrogen bond to the carbonyl oxygen O2 of a neighboring molecule. N2 and N3 form hydrogen bonds to Br4 of the intercalated tetrabromoaurate anion, Au2. The charge balance hydrogen atom, bonded to O1 forms a hydrogen bond to O3 of a neighboring molecule (see Table of Hydrogen Bonds for details).

No unusual bond distances or angles are observed within the molecules.

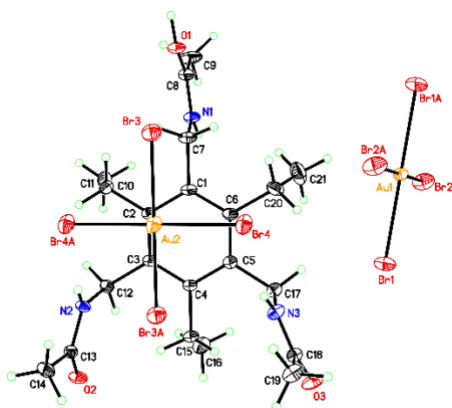


Figure S16. Atomic displacement plot and labeling scheme for **2**•HAuBr₄. Displacement ellipsoids depicted at 50% probability level and hydrogen atoms as spheres of an arbitrary radius.

Crystal data and structure refinement for **2•HAuBr₄**.

Identification code	nd1904
Empirical formula	C ₂₁ H ₃₄ AuBr ₄ N ₃ O ₃
Formula weight	893.12
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /n
Unit cell dimensions	$a = 12.5789(11)$ Å $\alpha = 90^\circ$ $b = 17.0609(15)$ Å $\beta = 103.800(2)^\circ$ $c = 13.3931(12)$ Å $\gamma = 90^\circ$
Volume	2791.3(4) Å ³
Z	4
Density (calculated)	2.125 g.cm ⁻³
Absorption coefficient (μ)	11.023 mm ⁻¹
F(000)	1696
Crystal color, habit	orange, block
Crystal size	0.189 × 0.149 × 0.088 mm ³
θ range for data collection	1.969 to 30.649°
Index ranges	-18 ≤ h ≤ 17, -24 ≤ k ≤ 24, -19 ≤ l ≤ 19
Reflections collected	99093
Independent reflections	8616 [R _{int} = 0.0379]
Completeness to $\theta = 25.242^\circ$	100.0 %
Absorption correction	Numerical
Max. and min. transmission	0.6116 and 0.2843
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8616 / 0 / 310
Goodness-of-fit on F ²	1.022
Final R indices [I > 2 σ (I)]	R ₁ = 0.0211, wR ₂ = 0.0438
R indices (all data)	R ₁ = 0.0373, wR ₂ = 0.0485
Extinction coefficient	n/a
Largest diff. peak and hole	1.536 and -1.161 e ⁻ .Å ⁻³

D. Hydrogen Bond Information

Table S1. Summary of individual hydrogen bond distances (Å) and angles (°) observed for complexes of **1** and **2** with H AuX₄.

	N-H...X distance	N-H distance	H...X distance	N-H...X angle
1 •HAuCl ₄	3.332(3)	0.75(4)	2.66(4)	151(4)
	3.640(3)		3.04(4)	139(3)
	3.530(3)	0.83(3)	3.08(4)	116(3)
	3.306(3)		2.47(3)	174(3)
	3.548(3)	0.85(4)	3.04(4)	121(3)
	3.534(3)		2.70(4)	168(4)
1 •HAuBr ₄	3.56(2)	0.88	2.693	167
	3.79(2)		3.245	122
	3.89(2)	0.88	3.339	123
	3.46(2)		2.601	164
	3.75(2)	0.88	3.375	109
	3.60(2)		2.727	171
2 •HAuCl ₄	3.581(2)	0.88(3)	3.05(3)	120(2)
	3.371(2)		2.50(3)	169(2)
	3.572(2)	0.82(2)	3.19(2)	111(2)
	3.364(2)		2.55(2)	173(2)
2 •HAuBr ₄	3.657(2)	0.80(3)	3.30(3)	110(2)
	3.492(2)		2.70(3)	174(3)
	3.678(2)	0.82(3)	3.15(4)	124(3)
	3.530(2)		2.73(3)	165(3)

E. Conformations

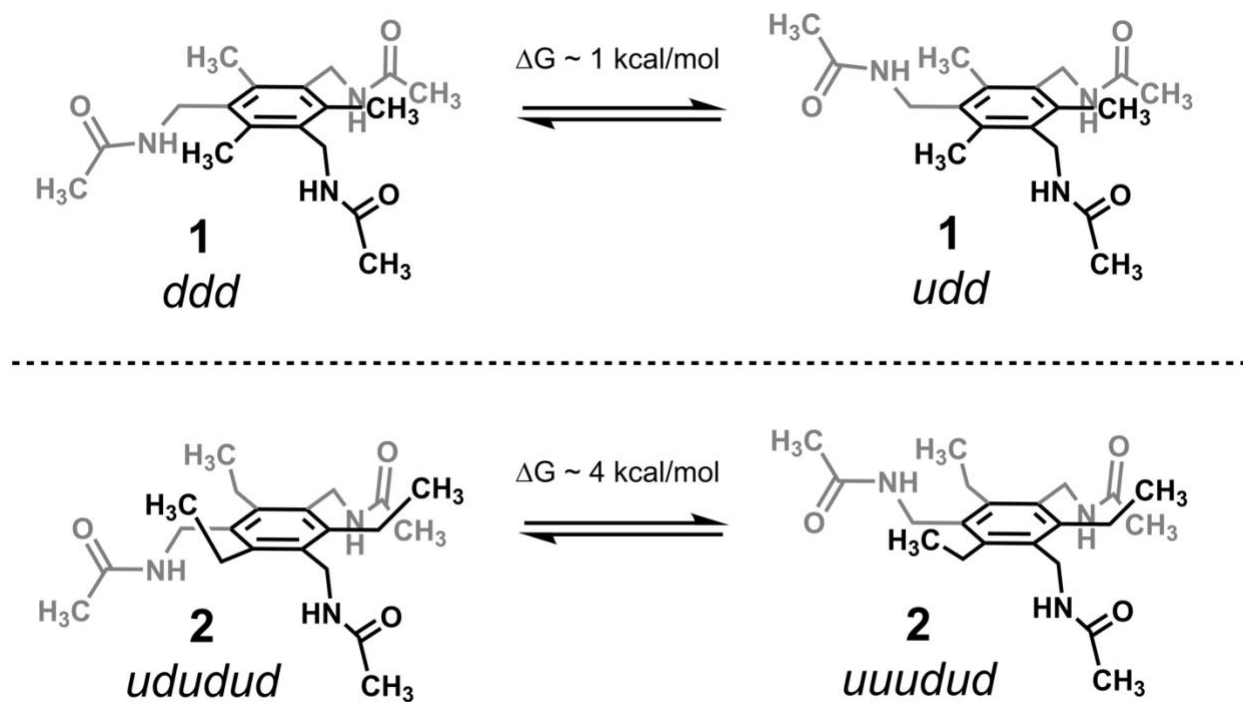


Figure S17. ΔG for conversion of the lowest energy conformation of **1** or **2** into the high energy conformation observed in the solid state. Each substituent on the aryl ring is either *d* = down or *u* = up.

F. References

- 1 A. K. Mishra and S. Verma, *Inorg. Chem.*, 2010, **49**, 3691–3693.
- 2 K. J. Wallace, R. Hanes, E. Anslyn, J. Morey, K. V Kilway and J. Siegel, *Synthesis*, 2005, **12**, 2080–2083.
- 3 *APEX-III*. Bruker AXS. Madison, Wisconsin, USA. **2016**.
- 4 L. Krause, R. Herbst-Irmer, G. M. Sheldrick and D. Stalke, *J. Appl. Crystallogr.*, 2015, **48**, 3–10.
- 5 G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3–8.
- 6 G. M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3–8.
- 7 A. L. Spek. *Acta Cryst.*, **2009**, *D65*, 148.