Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Symmetry-driven diastereoselective functionalization of simple trianglamine

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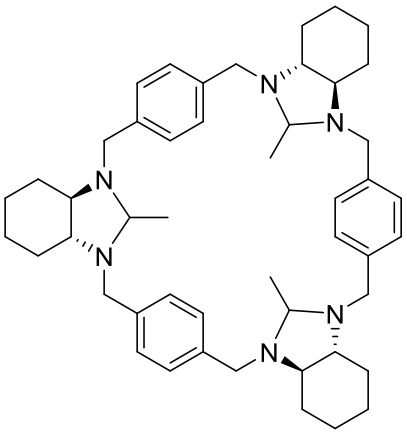
^{1}H and $^{13}C\{H\}$ NMR spectra were recorded on Bruker Ascend 600 MHz or Bruker Ultrashield 300 MHz spectrometer at room temperature. Chemical shifts are reported in parts per million (ppm). Spectra are referenced using an internal reference (TMS or $CDCl_3$ residual solvent peak). Data are described as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad) and integration. Melting points were measured on the BUCHI B-545. High resolution mass spectra (HRMS) were measured on the Bruker Impact HD. Optical rotations were recorded on the Jasco P-2000 polarimeter at 20 °C. ECD and UV spectra were measured using the Jasco J-810 spectropolarimeter.

Synthesis of **3a-c**

General procedure:

To a solution of trianglamine (324 mg, 0.5 mmol) in ethanol (18 mL) was added aldehyde (7 mmol). The mixture was stirred for 20 h at rt, then the precipitated solid (68-80%) was filtered and washed with ethanol. The crude product was purified by crystalization from a 1:2 mixture of dichloromethane-ethanol.



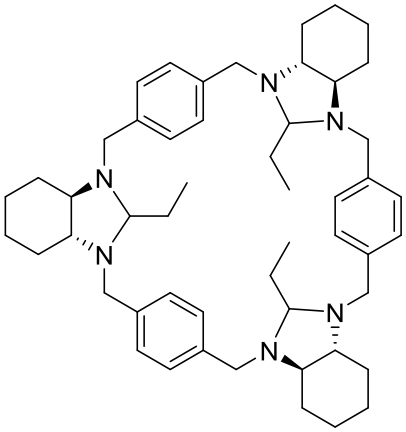
3a. Crystalline solid; yield 190 mg (52%); mp 238-240 °C (decomp); $[\alpha]_D^{20}$-76° (*c* 1.025, CH_2Cl_2);

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.95 (d, *J* = 8.2 Hz, 6H), 6.93 (d, *J* = 8.2 Hz, 6H), 3.80 (d, *J* = 13.6 Hz, 3H), 3.68 (d, *J* = 13.6 Hz, 3H), 3.55 – 3.59 (m, 6H), 3.26 (d, *J* = 13.0 Hz, 3H), 2.65 – 2.61 (m, 3H), 2.53-2.49 (m, 3H), 2.22 (d, *J* = 12.6 Hz, 3H), 2.02 (d, *J* = 7.1 Hz, 3H), 1.87 (d, *J* = 6.5 Hz, 6H), 1.35-1.21 (m, 12H), 0.77 (d, *J* = 5.9 Hz, 9H) ppm;

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 138.1, 134.8, 130.1, 128.8, 74.2, 63.9, 63.6, 53.4, 51.1, 29.6, 28.1, 24.9, 24.5, 19.1 ppm;

ATR-IR: 2925 (CH_{asym}), 2854 (CH_{sym}), 2801 (C-N $_{strench}$),1513 (C-C=C $_{arom}$), 1444 ($CH_{2\ def}$), 1381, 1363, 1348 (CH_{def}), 1223 (C-C-N $_{bending}$), 1174, 1146 (CH_{def}), 1113, 1079, 837 (Ar-H $_{def}$) cm^{-1};

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{48}H_{67}N_6$ 727.5422. Found 727.5415.



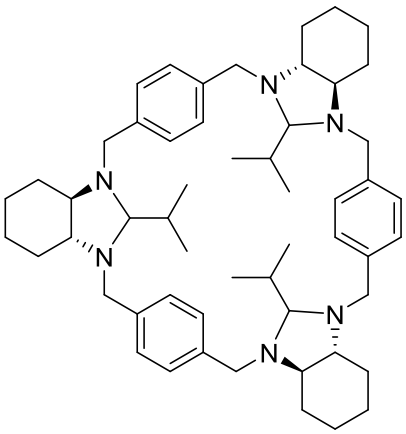
3b. Crystalline solid; yield 230 mg (60%); mp 215-221 °C; $[\alpha]_D^{20}$-31° (*c* 1.015, CH_2Cl_2);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.00 (d, *J* = 8.1 Hz, 6H), 6.95 (d, *J* = 7.8 Hz, 6H), 3.88 (d, *J* = 13.3 Hz, 3H), 3.65 (dd, *J* = 16.6, 12.8 Hz, 6H), 3.31 (dd, *J* = 6.5, 4.1 Hz, 3H), 3.14 (d, *J* = 12.4 Hz, 3H), 2.70 (m, 3H), 2.61 (td, *J* = 10.3, 3.4 Hz, 3H), 2.21 (d, *J* = 13.6 Hz, 3H), 2.05 (d, *J* = 13.4 Hz, 3H), 1.88-1.85 (m, 6H), 1.44 (qd, *J* = 11.8, 3.4 Hz, 3H), 1.32 (t, *J* = 9.5 Hz, 6H), 1.25-1.19 (m, 3H), 1.15-1.08 (m, 3H), 0.94-0.87 (m, 3H), 0.37 (t, *J* = 7.4 Hz, 9H) ppm;

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 138.49, 136.44, 129.98, 129.68, 80.32, 65.28, 64.10, 55.78, 52.46, 30.46, 28.18, 28.16, 25.44, 24.78, 10.33 ppm;

ATR-IR: 2925 (CH_{asym}), 2858 (CH_{sym}), 2810 (C-N $_{strench}$), 1511 (C-C=C $_{arom}$), 1433 ($CH_{2\ def}$), 1378, 1351, 1336 (CH_{def}), 1223 (C-C-N $_{bending}$), 1172, 1141 (CH_{def}), 1117, 1100, 1068, 863, 807 (Ar-H $_{def}$) cm^{-1};

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{51}H_{73}N_6$ 769.5891. Found 769.5892.



3c. Crystalline solid; yield 235 mg (57%); mp 209-212 °C; $[\alpha]_D^{20}$-24° (*c* 1.015, CH_2Cl_2);

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.0 Hz, 6H), 7.05 (d, *J* = 7.9 Hz, 6H), 4.01 (d, *J* = 13.1 Hz, 3H), 3.76 (d, *J* = 12.1 Hz, 3H), 3.68 (d, *J* = 13.1 Hz, 3H), 3.31 (d, *J* = 4.8 Hz, 3H), 3.14 (d, *J* = 12.1 Hz, 3H), 2.76-2.69 (m, 6H), 2.21 (d, *J* = 12.2 Hz, 3H), 2.04 (d, *J* = 12.1 Hz, 3H), 1.84 (dd, *J* = 19.0, 5.3 Hz, 6H), 1.55-1.49 (m, 3H), 1.32-1.20 (m, 9H), 1.06-1.00 (m, 3H), 0.57 (d, *J* = 6.9 Hz, 9H), 0.18 (d, *J* = 6.8 Hz, 9H) ppm;

$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) δ 138.5, 137.5, 130.2, 129.7, 85.1, 66.3, 64.7, 58.2, 53.8, 33.7, 30.9, 28.0, 25.7, 24.7, 19.5, 18.4 ppm;

ATR-IR: 2925 (CH_{asym}), 2858 (CH_{sym}), 2819(C-N $_{strench}$), 1511 (C-C=C $_{arom}$), 1446 ($CH_{2\ def}$), 1383, 1354, 1335 (CH_{def}), 1223 (C-C-N $_{bending}$), 1166, 1141 (CH_{def}), 1105, 1071, 1022, 861, 811 (Ar-H $_{def}$) cm^{-1};

HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{54}H_{79}N_6$ 811.6361. Found 811.6386.

Table S1. Concentrations (*c*, in mol L^{-1}) of the samples used for UV and ECD measurements.

Compound	*c* (cyclohexane)
3a	1.377×10^{-4}
3b	1.308×10^{-4}
3c	1.234×10^{-4}

Table S2. ECD ($\Delta\varepsilon$, in $dm^3\cdot mol^{-1}\cdot cm^{-1}$) and UV ($\varepsilon$, in $dm^3\cdot mol^{-1}\cdot cm^{-1}$) data for derivatives **3a-c** measured in cyclohexane solution[a].

Compound	$\Delta\varepsilon$ (nm)	ε (nm)[b]
3a	5.49 (228.5); –13.13 (208); –13.29 (198.5); 12.33 (193); –3.37 (187)	102100 (190.5)
3b	3.63 (228); –29.34 (198.5); 34.76 (192); 14.74 (185)[c]	149000 (190.5)
3c	–6.41 (208.5); –19.17 (197.5); 23.51 (192); 10.19 (185)[c]	150100 (191.5)

[a]The concentration of analytes ranged from 1.01 to 1.38×10^{-4} mol L^{-1}. The spectra were recorded in pure cyclohexane, from 450 to 185 nm, with a scan speed of 100 nm min^{-1} and 4 accumulations. [b]Only well-established absorption bands of ε > 40000 were reported. [c]End of measuring range.

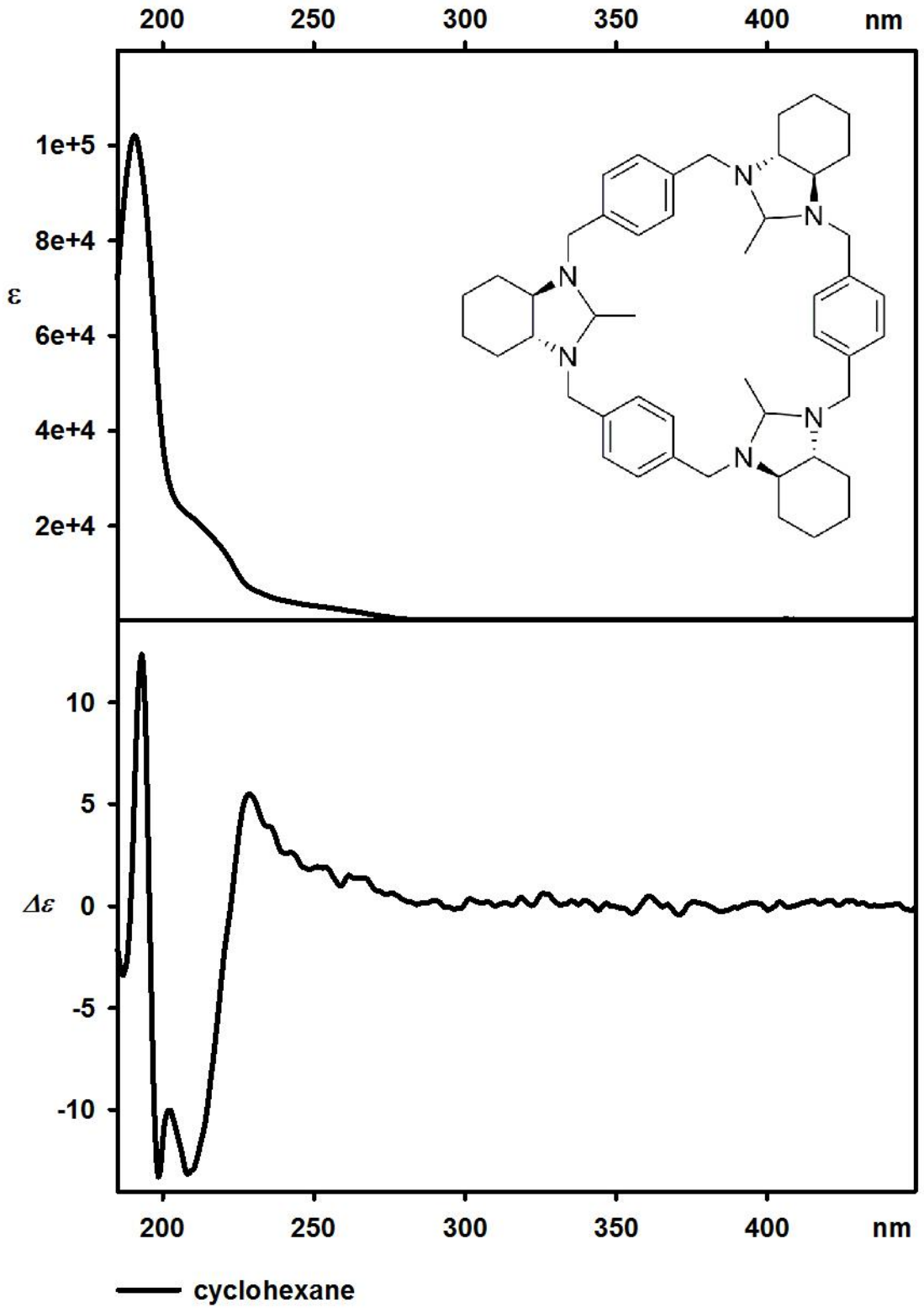


Figure S1. CD and UV spectra of **3a**.

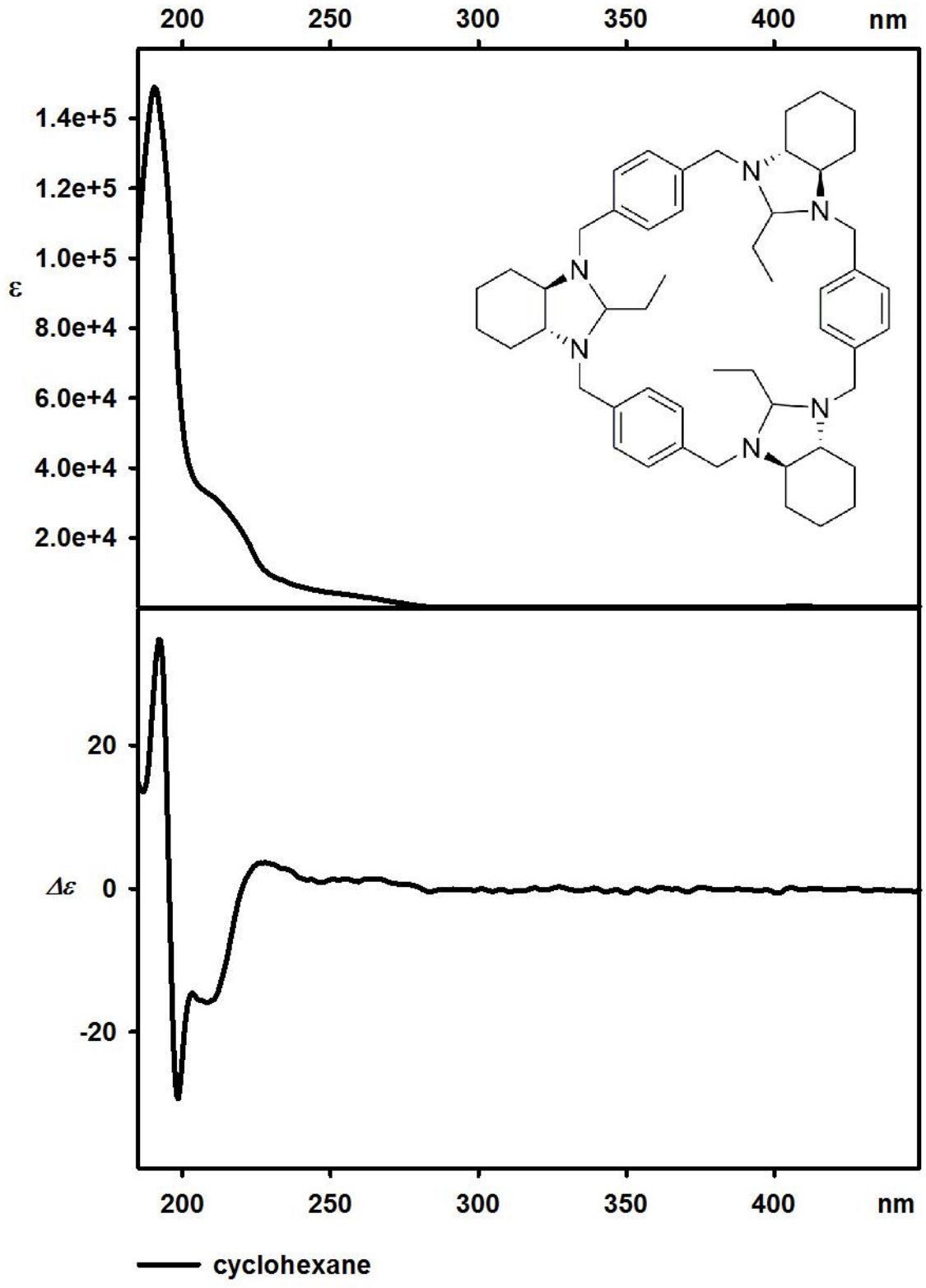


Figure S2. CD and UV spectra of **3b**.

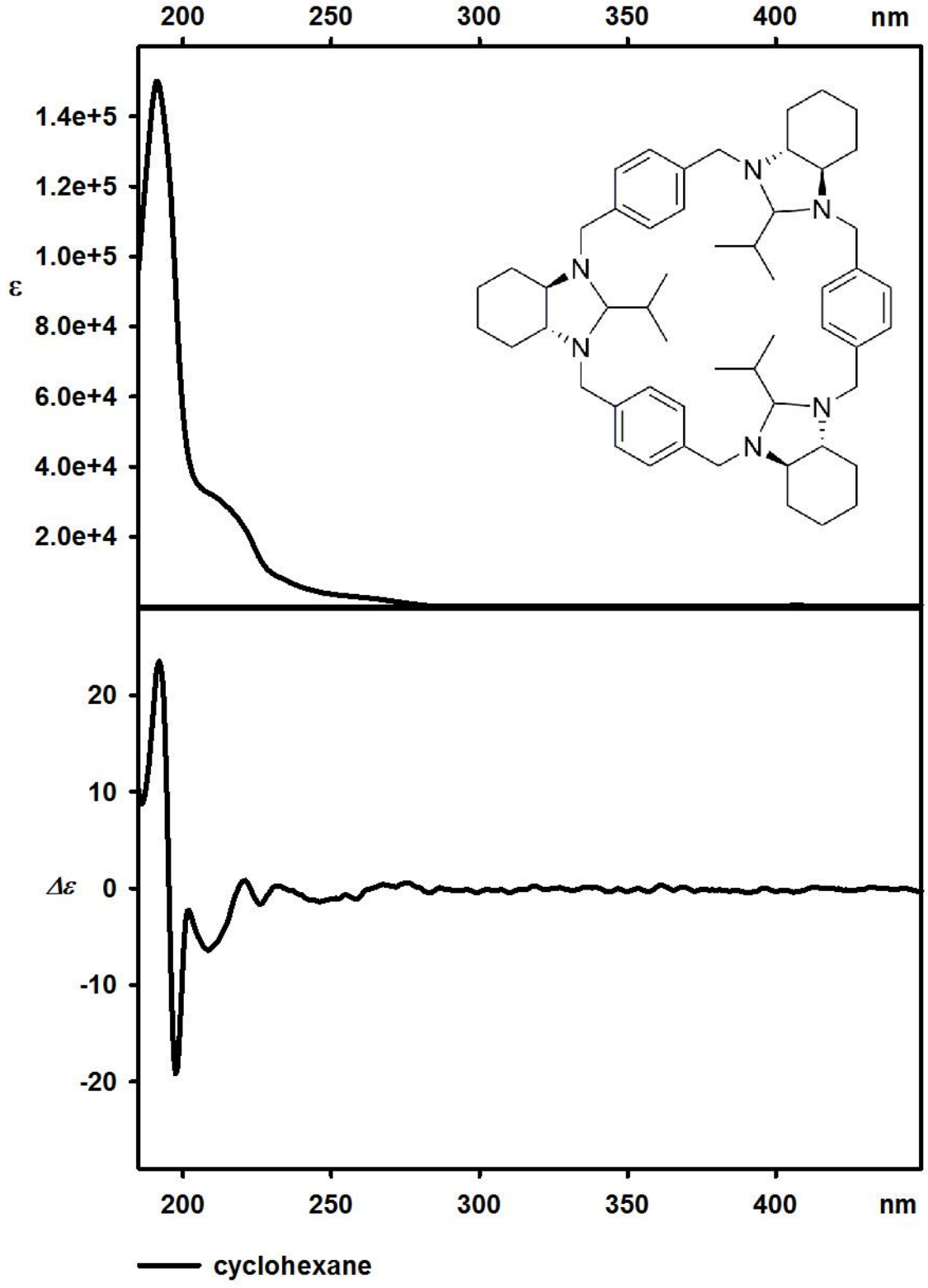


Figure S3. CD and UV spectra of **3c**.

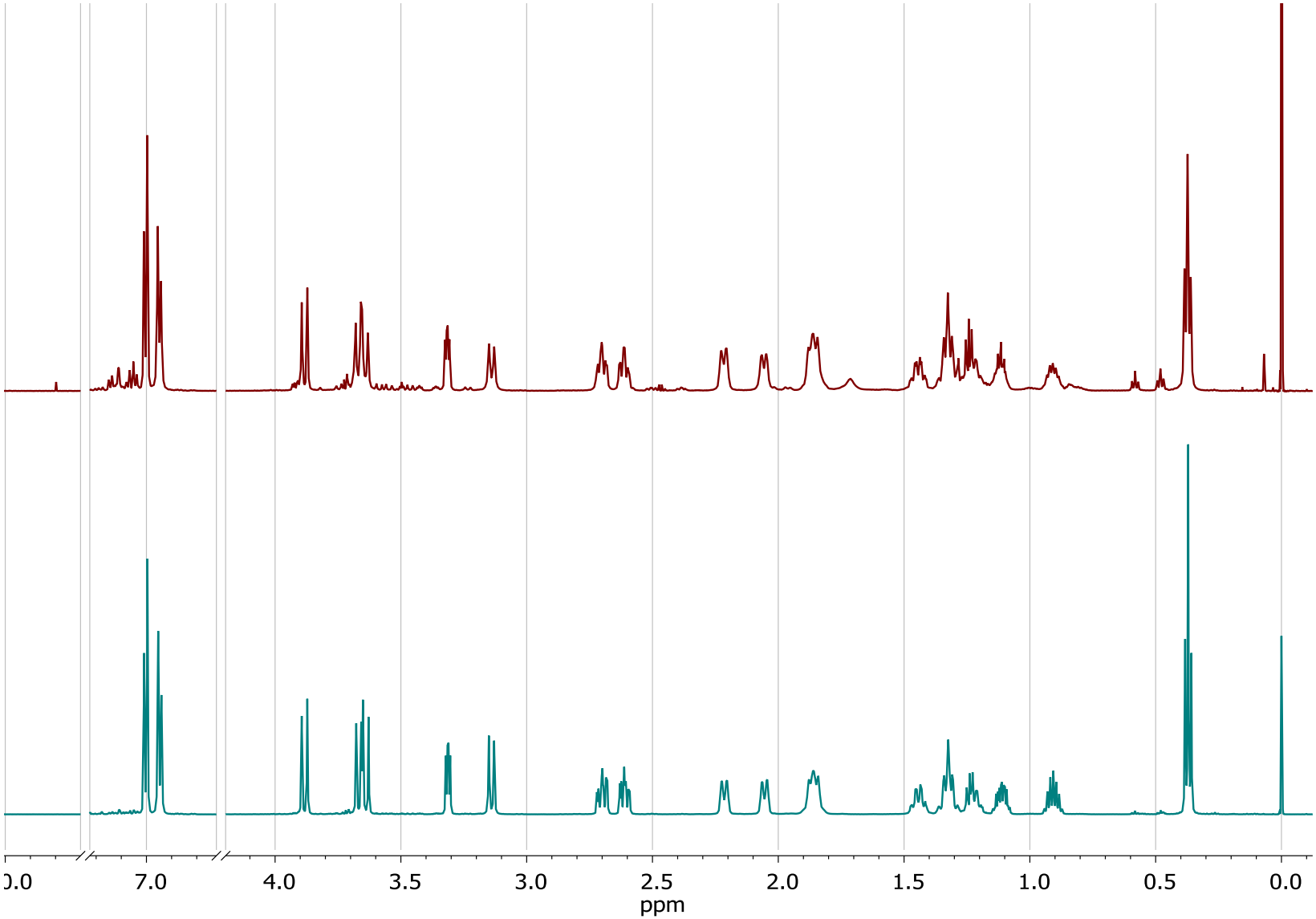


Figure S4. ^{1}H NMR spectra of crude product (top) and crystallized (bottom) of **3b**.

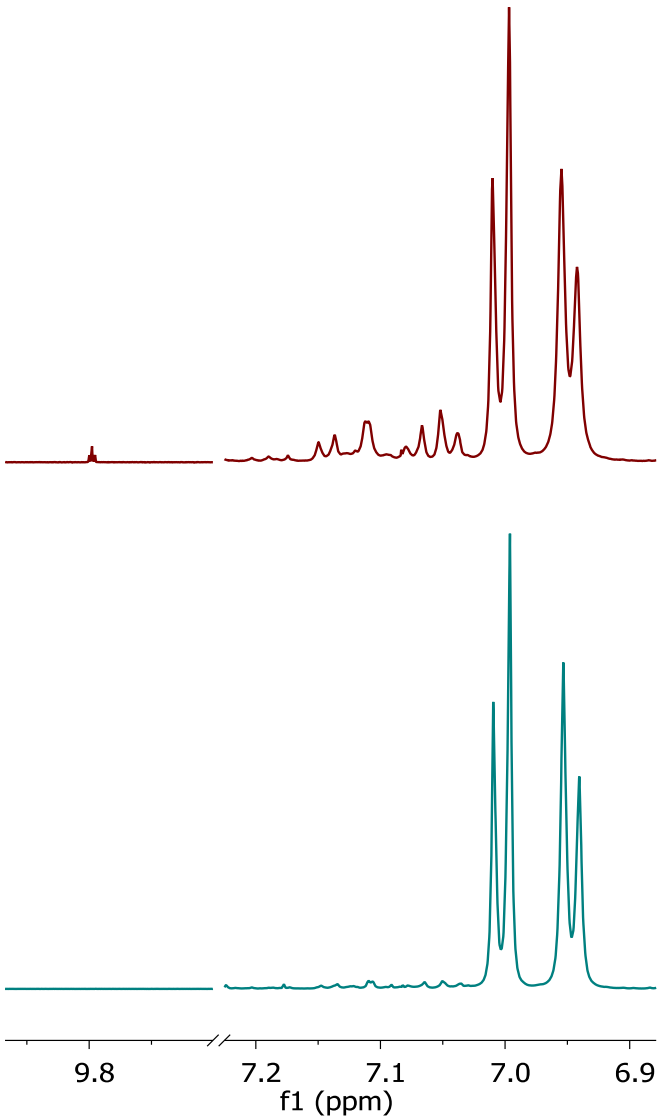


Figure S5. Part of the ^{1}H NMR spectra of crude product (top) and crystallized (bottom) of **3b**.

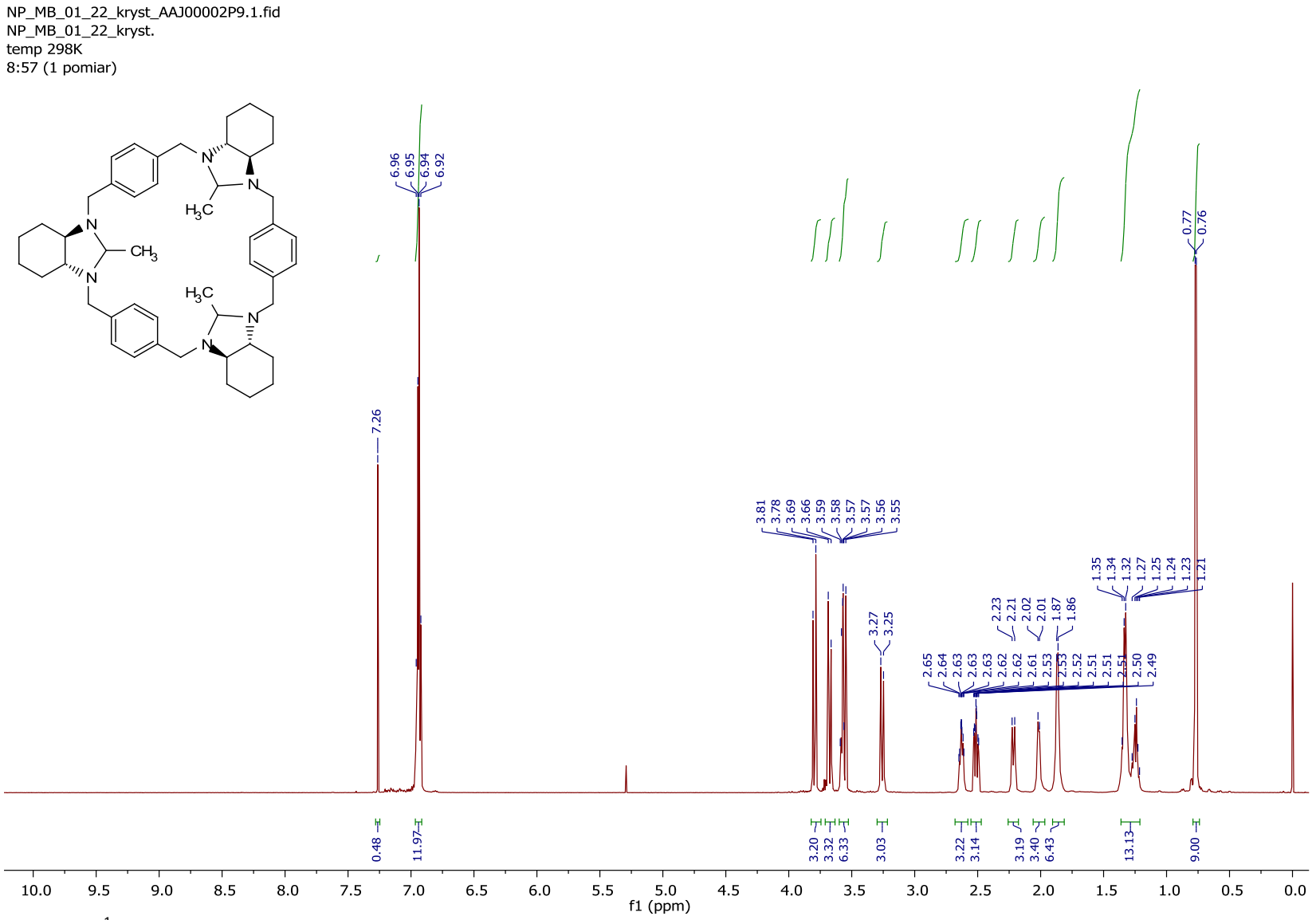


Figure S6. ^{1}H NMR spectrum of crystallized **3a** in $CDCl_3$.

NP_MB_01_22_kryst_AAJ00002P9.2.fid
NP_MB_01_22_kryst.
temp 298K

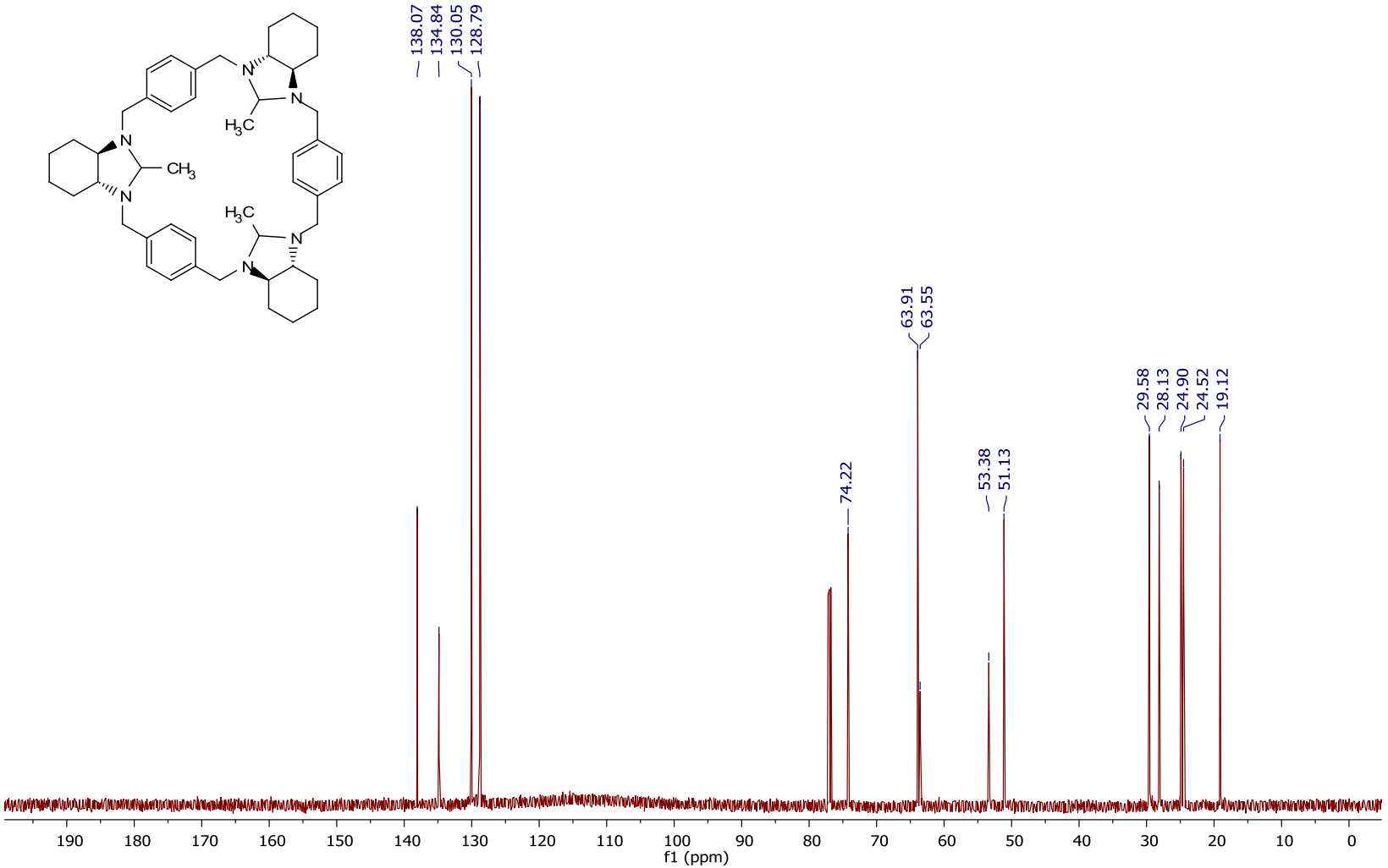


Figure S7. ^{13}C NMR spectrum of crystallized **3a** in $CDCl_3$.

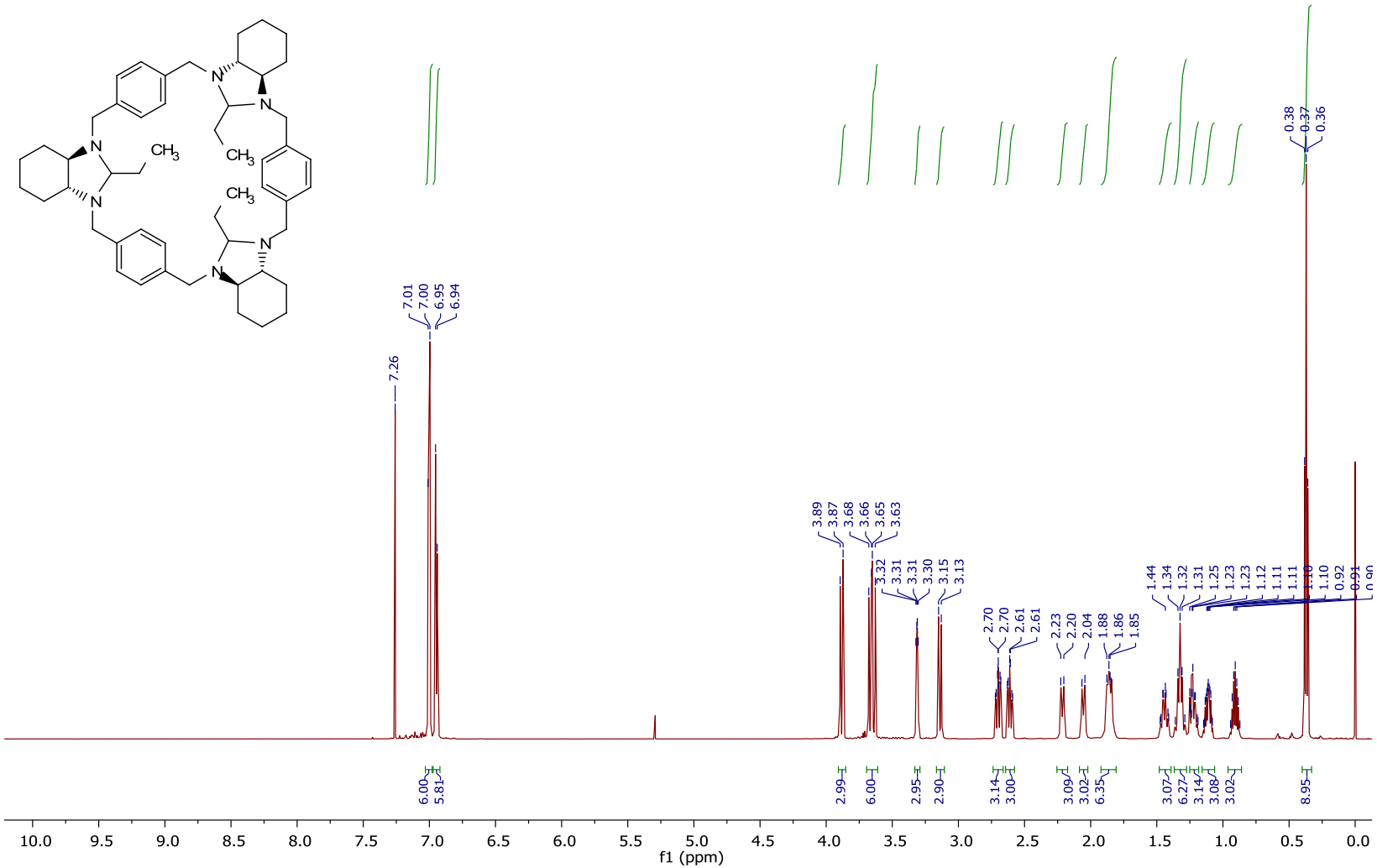


Figure S8. ^{1}H NMR spectrum of crystallized **3b** in $CDCl_3$.

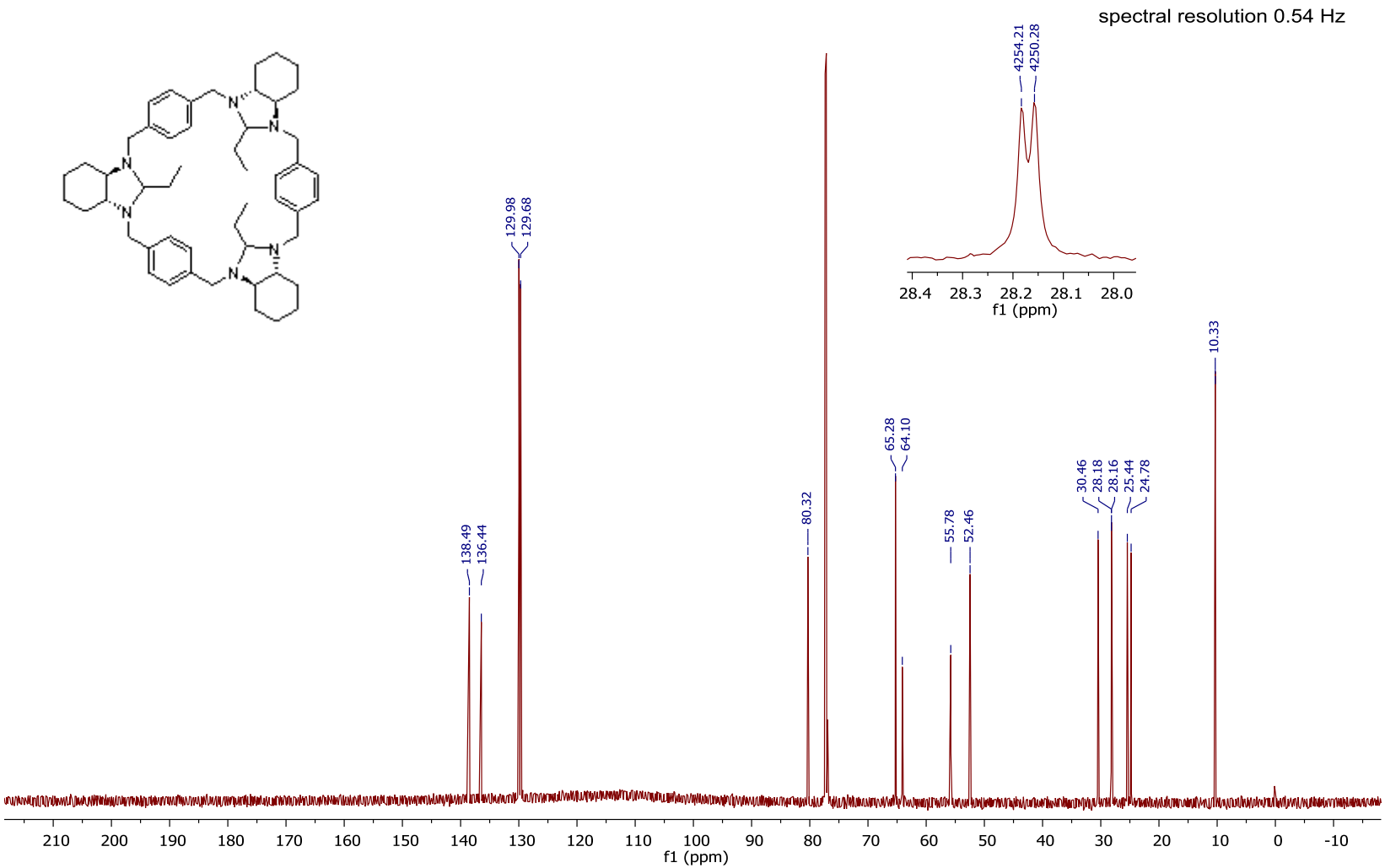


Figure S9. ^{13}C NMR spectrum of crystallized **3b** in $CDCl_3$.

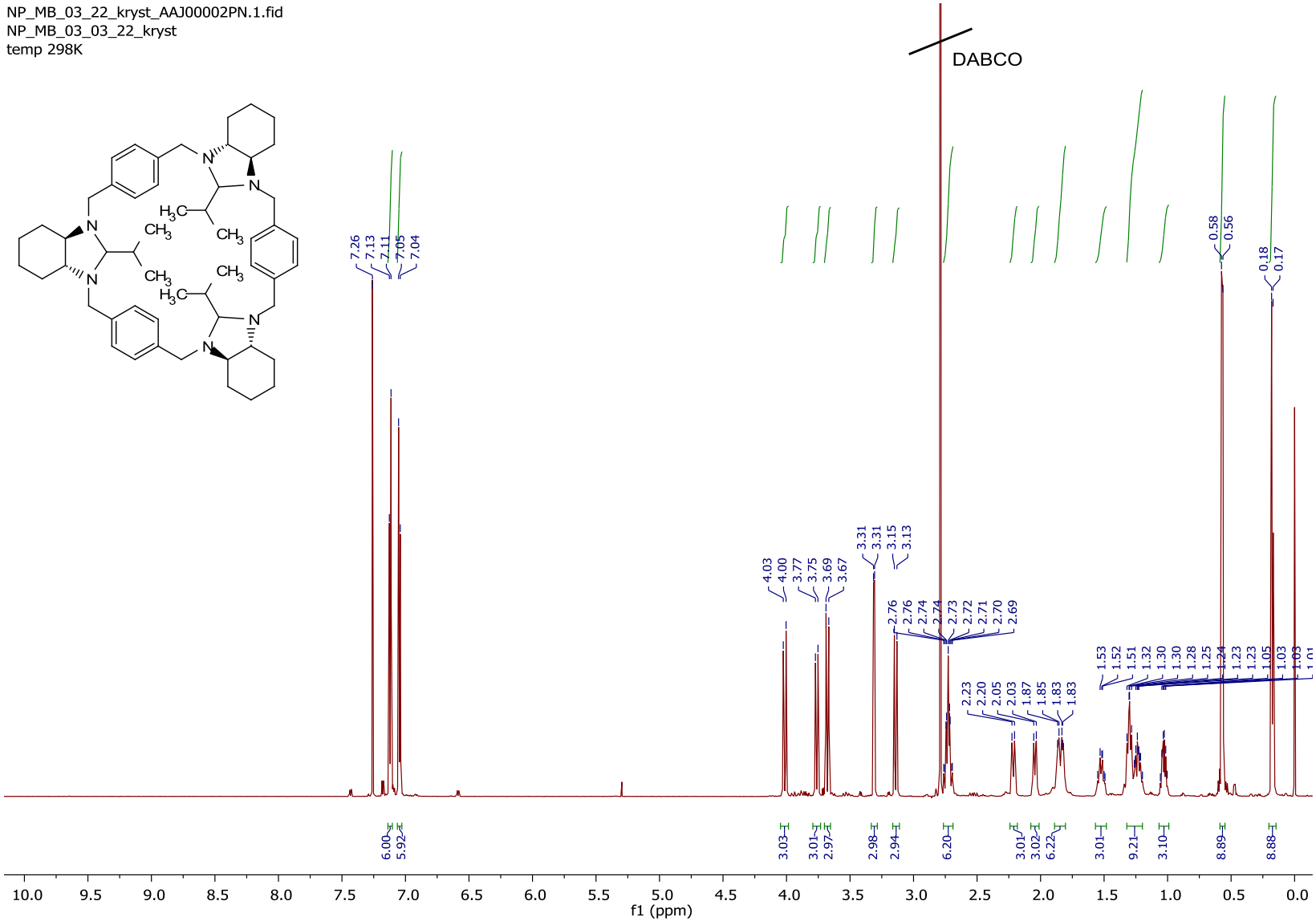
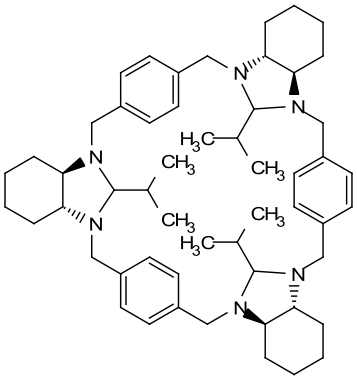


Figure S10. ^{1}H NMR spectrum of crystallized **3c** with DABCO addition.

NP_MB_03_22_kryst_AAJ00002PN.2.fid
NP_MB_03_03_22_kryst
temp 298K



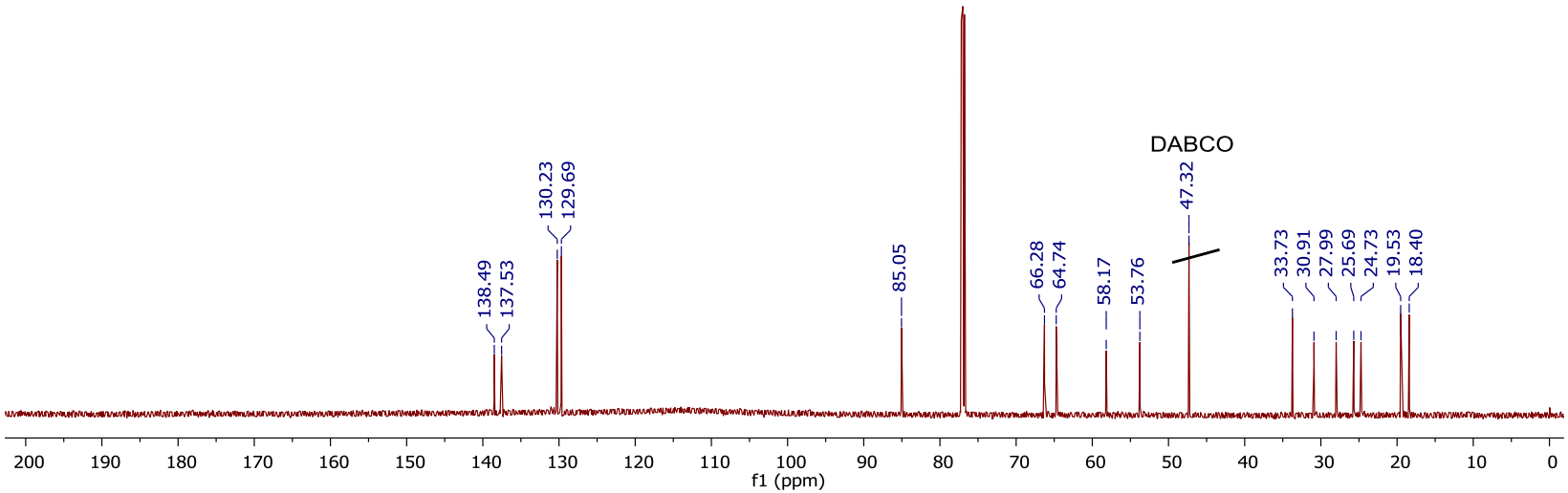


Figure S11. ^{13}C NMR spectrum of crystallized **3c** with DABCO addition.

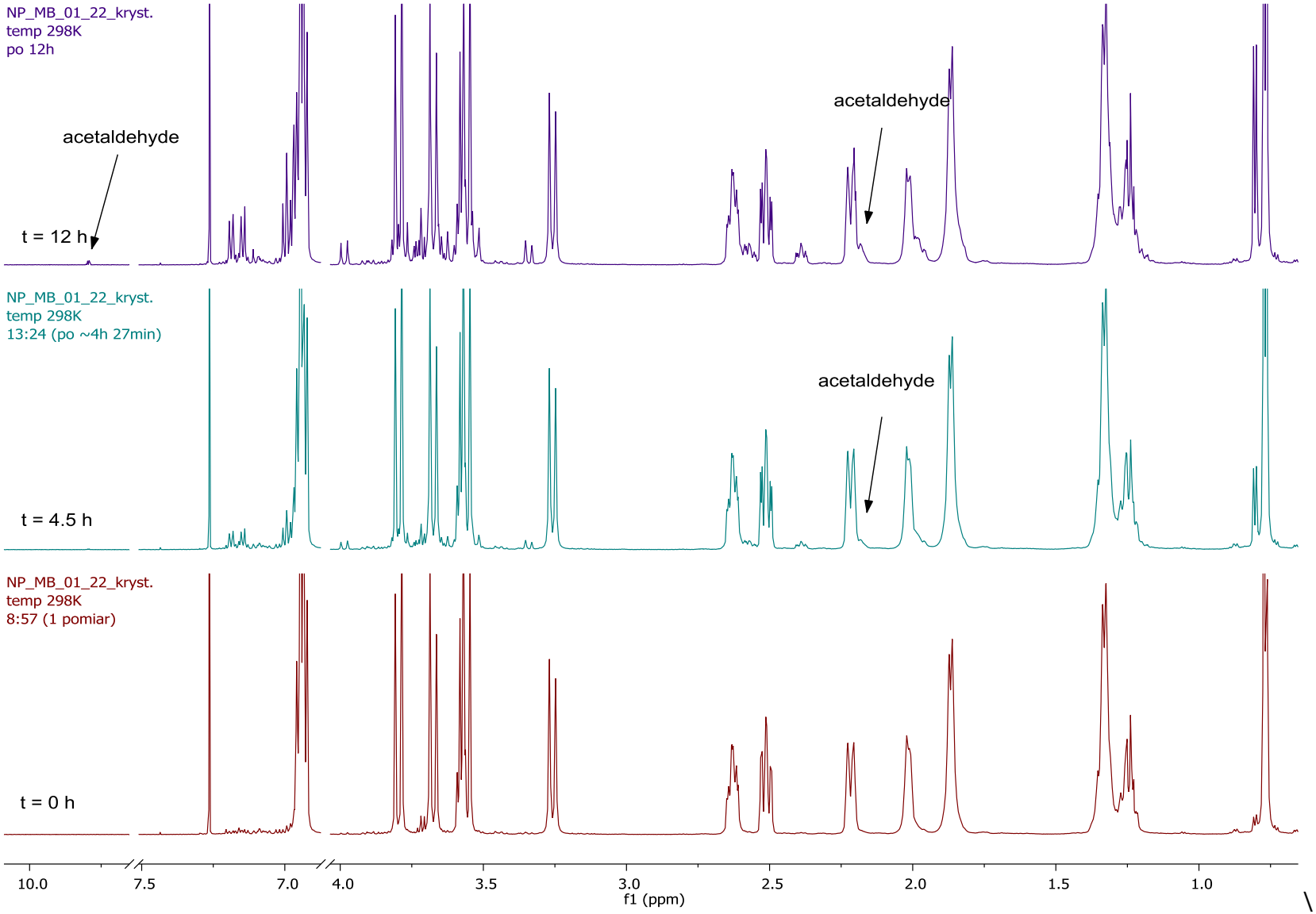


Figure S12. Time-dependent ^{1}H NMR spectrum of crystallized **3a** in $CDCl_3$.

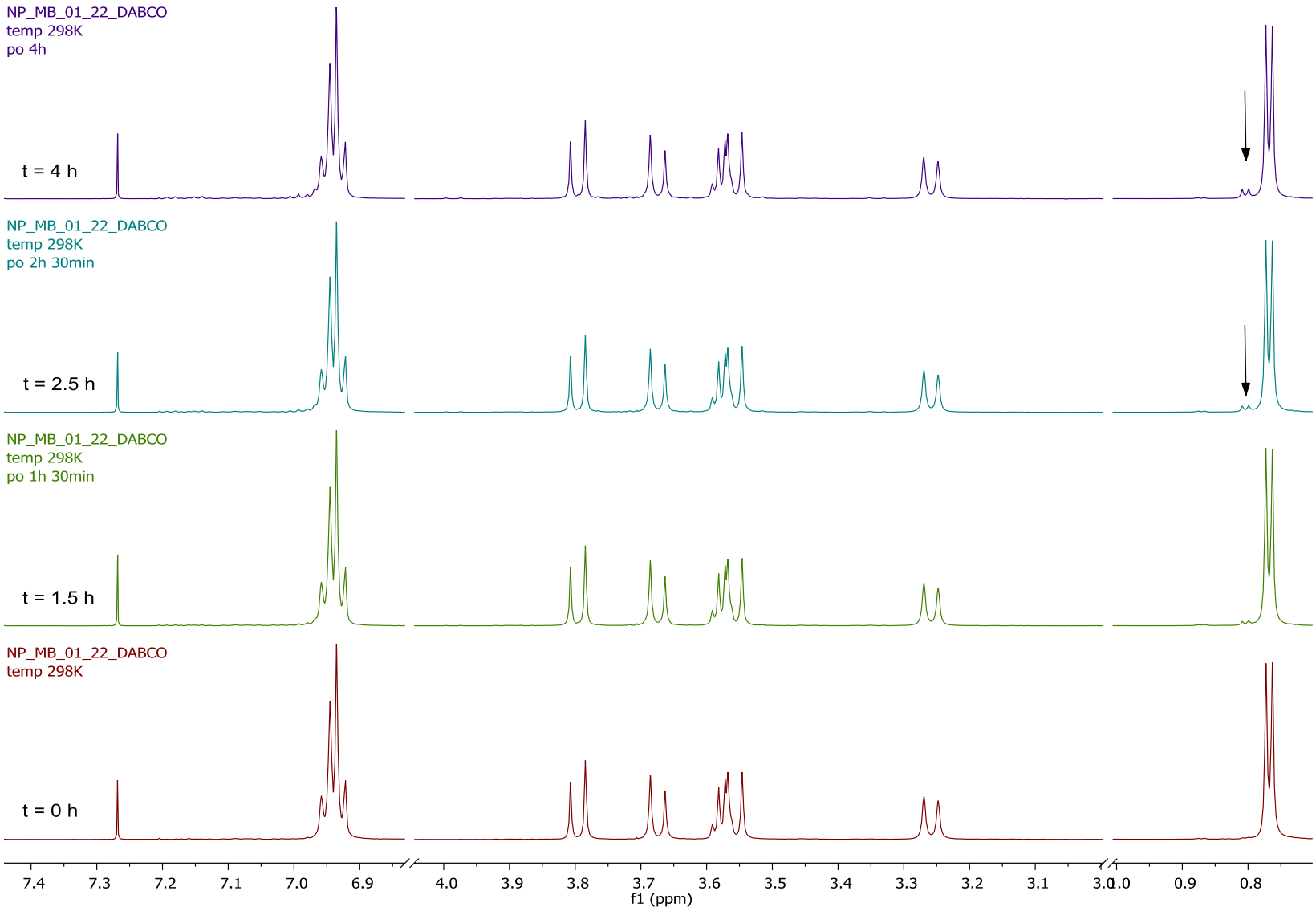


Figure S13. Time-dependent ^{1}H NMR spectrum of crystallized **3a** in $CDCl_3$ with DABCO addition.

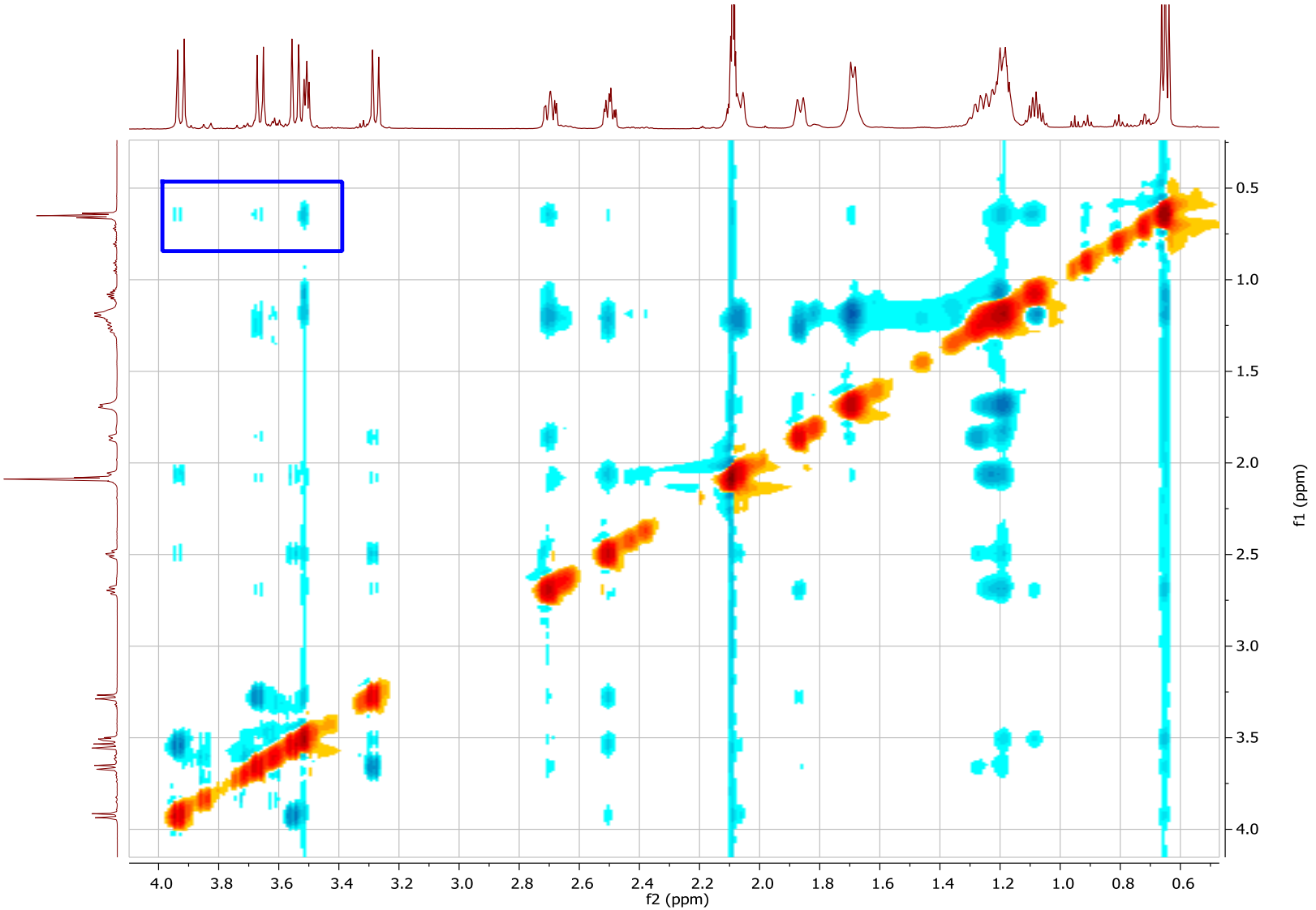


Figure S14. NOESY of **3b** in toluene-d_8.

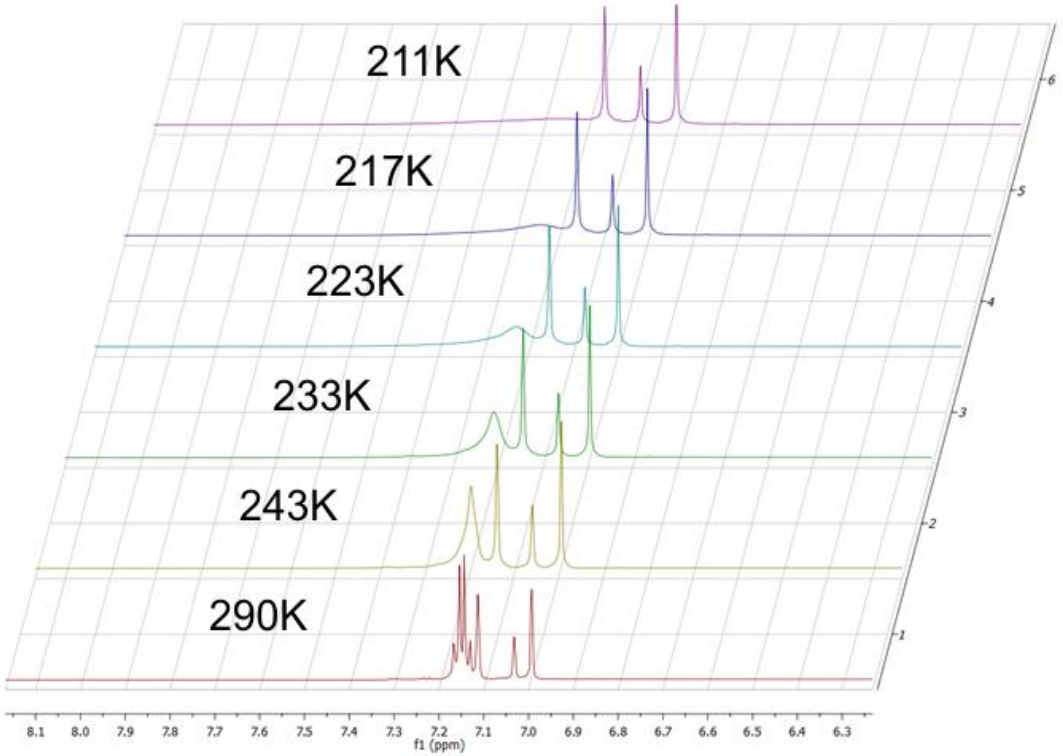


Figure S15. Low temperature NMR spectra of **3b**.

Single-Crystal X-ray diffraction

Crystals suitable for single-crystal X-ray diffraction were obtained from slow evaporation of *p*-xylene (**3a**), a mixture of dichloromethane and ethanol (**3b**) and *m*-xylene (**3c**).

Intensity data collected for **3a** and **3c** was measured on an Xcalibur diffractometer equipped with a graphite monochromator and MoKα radiation (λ = 0.71073 Å). The data for **3b** was collected on a SuperNova diffractometer equipped with Cu microfocus source (λ=1.54178 Å) and 135 mm Atlas CCD detector. Data reduction and analysis for all of the crystals were carried out with the CrysAlisPro program.[1] In all experiments the sample temperature was controlled with an Oxford Instruments Cryosystem cold nitrogen-gas blower. The structures were solved by direct methods using SHELXT [2] or SIR-2011,[3] and refined by the full-matrix least-squares techniques within SHELXL.[2] Crystals of **3b** found to be twinned. The twin analysis performed with the CrysAlisPro [1] identified two triclinic domains. This was expressed by the matrix (-100, 0-10, 001), which corresponds to a rotation of 179.5° about the [001] direct lattice direction. Subsequent refinement indicated that the twin fraction of the second domain was 0.479(1). All heavy atoms were refined anisotropically. The hydrogen atoms bound to C atoms were placed at calculated positions and refined using a riding model, and their isotropic displacement parameters were given a value 20% higher than the isotropic equivalent for the atom to which the H atoms were attached (for methyl hydrogens this value has been increased to 50%).

Owing to the Flack parameter [4] was meaningless, the absolute structure of the investigated crystals was assumed from the known absolute configuration of the (*R*,*R*)-1,2-diaminecyclohexane which was used as a starting material in the syntheses. Crystals of **3a** grew as needles and gave weak diffraction data beyond sin(theta)/lambda > 0.5 (i.e. low resolution) hence the low ratio observed to unique reflection and low bonds precision. Graphical images were produced in Xseed [5] using Pov-Ray [6] and Mercury [7] programs. The solvent accessible volumes shown as pink Connolly surface [8] were calculated using a probe radius of 1.5Å. The relevant crystal data and refinement parameters are listed in Table S3.

CCDC 2184538-2184540 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data%5Frequest/cif

Table S3. Crystal data and structure refinement parameters for crystal investigated **3a-c**.

	3a	**3b**	**3c**
Crystal data			
Chemical formula	$C_{48}H_{66}N_6$	$C_{51}H_{72}N_6$	$C_{54}H_{78}N_6$, C_8H_{10}
M_r	727.06	769.14	917.38
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Triclinic, $P1$	Monoclinic, $P2_1$
T (K)	100	130	100
a, b, c (Å)	5.4394(9), 25.596(5), 30.105(7)	9.4631(7), 12.7155(11), 19.2980(7)	16.4016(6), 7.9236(2), 21.2919(7)
α, β, γ (°)	90, 90, 90	86.280(5), 89.524(4), 87.865(7)	90, 98.009(3), 90
V (Å^3)	4191.5(15)	2315.5(3)	2740.10(15)
Z, Z'	4, 1	2, 2	2, 1
D_x [g/cm^3]	1.152	1.103	1.112
Radiation type	Mo $K\alpha$	Cu $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.07	0.49	0.07
Crystal size (mm)	0.60×0.12×0.09	0.30×0.20×0.05	0.60×0.34×0.06
Data collection			
Diffractometer	Xcalibur, Eos	SuperNova, Atlas	Xcalibur, Eos
Absorption correction	Multi-scan	Multi-scan	Multi-scan
T_{min}, T_{max}	0.122, 1.000	0.761, 1.000	0.912, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	14870, 7405, 2746	31289, 31289, 22796	29653, 12589, 9858
R_{int}	0.129	0.067	0.040
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.595	0.621	0.685
Refinement			
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.107, 0.289, 0.97	0.071, 0.208, 1.02	0.052, 0.106, 1.03
No. of reflections	7405	31289	12589
No. of parameters	490	1034	621
No. of restraints	0	3	1
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.32, -0.33	0.38, -0.27	0.21, -0.28
Absolute structure parameter	-4.2(10)	0.4(4)	0.5(10)

Computer programs: *SHELXL2014*/7 (Sheldrick, 2014).

Crystal 3a

Crystals of **3a** were obtained by slow evaporation from *p*-xylene solution at room temperature. The asymmetric unit, shown in Fig. S16 contains one molecule of **3a**. Although formal molecular symmetry is C_3, molecule **3a** is asymmetric in the crystal.

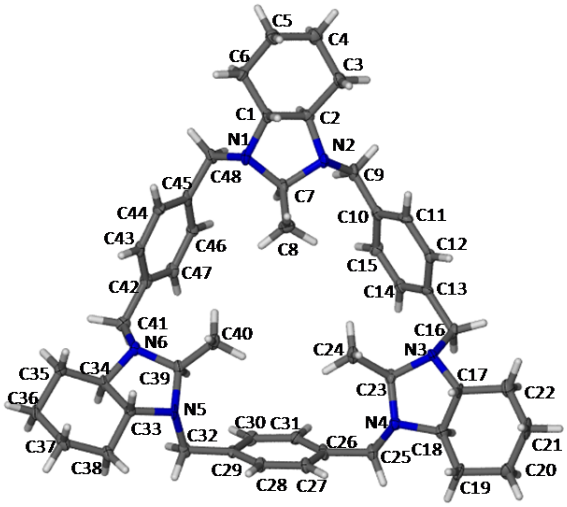


Figure S16. Asymmetric unit of **3a** together with labeling scheme. Ellipsoids are drawn at the 30% probability level, hydrogen atoms are represented by spheres of arbitrary radii.

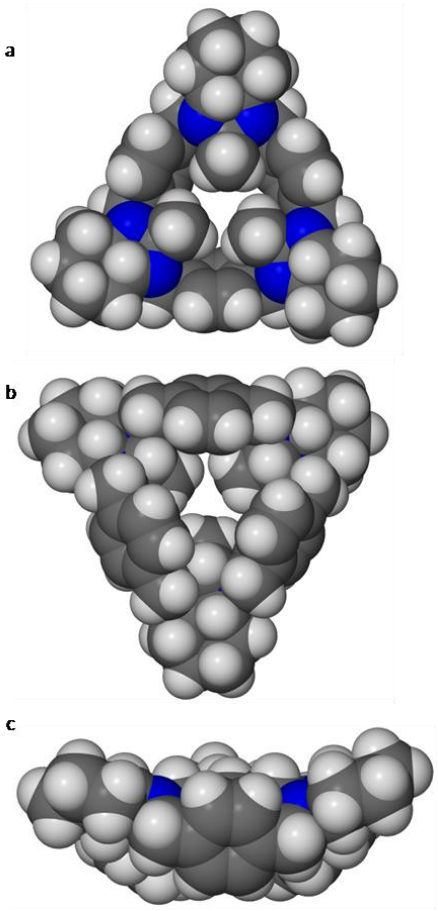


Figure S17. Molecular shape of **3a** illustrated in space-filling mode. Figures a, b and c represent a top, bottom and a side view of macrocycle, respectively.

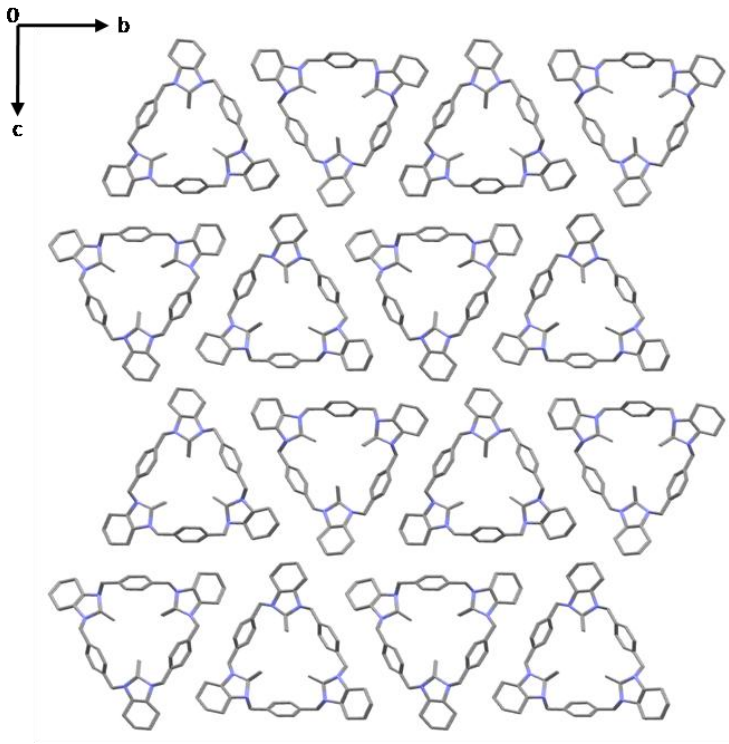


Figure S18. A packing diagram of **3a** as viewed along the *a* lattice direction. All H atoms are omitted for clarity.

Table S4. Selected torsion angles describing the conformation of macrocycle **3a**.

	Torsion angle [°]	Conformation
N1-C1-C2-N2	-41.3(10)	*G*$^-$
C1-C2-N2-C9	159.4(8)	*T*
C2-N2-C9-C10	168.1(9)	*T*
C13-C16-N3-C17	-168.0(8)	*T*
C16-N3-C17-C18	-99.8(9)	*A* (anticlinal)
N3-C17-C18-N4	-38.7(10)	*G*$^-$
C17-C18-N4-C25	161.2(8)	*T*
C18-N4-C25-C26	166.4(9)	*T*
C29-C32-N5-C33	-166.8(8)	*T*
C32-N5-C33-C34	-94.4(9)	*A* (anticlinal)
N5-C33-C34-N6	-41.1(9)	*G*$^-$
C33-C34-N6-C41	162.3(8)	*T*
C34-N6-C41-C42	163.0(9)	*T*
C45-C48-N1-C1	-168.7(9)	*T*
C48-N1-C1-C2	-96.2(10)	*A* (anticlinal)

Crystal 3b

Crystals of **3b** were obtained from slow evaporation of a mixture of dichloromethane and ethanol at room temperature. The asymmetric unit, shown in Fig. S19 contains two symmetry independent molecule of **3b**. Although formal molecular symmetry is C_3, none of symmetrically independent molecules of **3b** retain the symmetry in the crystal.

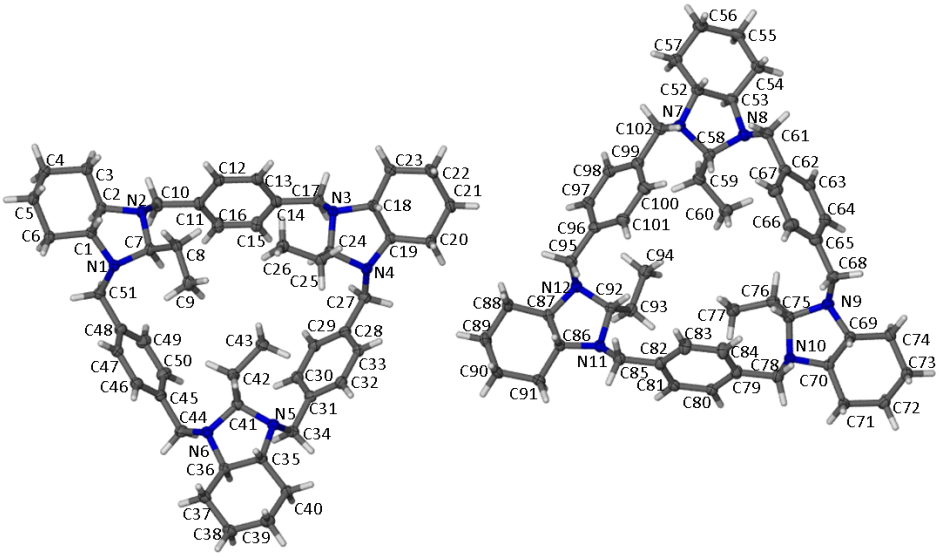


Figure S19. Asymmetric unit of **3b** together with labeling scheme. Ellipsoids are drawn at the 30% probability level, hydrogen atoms are represented by spheres of arbitrary radii.

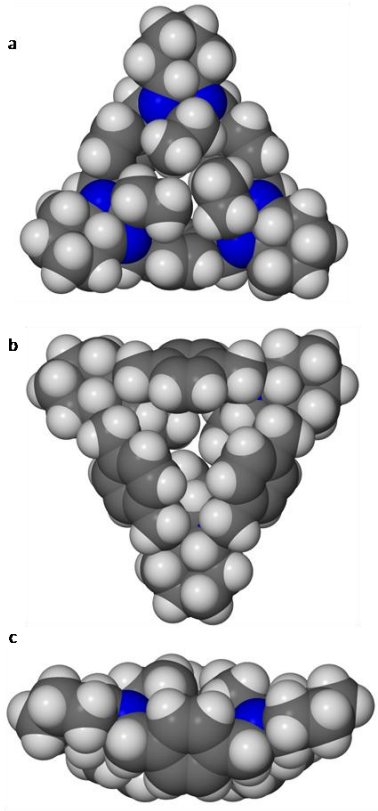


Figure S20. Molecular shape of **3b** illustrated in space-filling mode. Figures a, b and c represent a top, bottom and a side view of macrocycle, respectively.

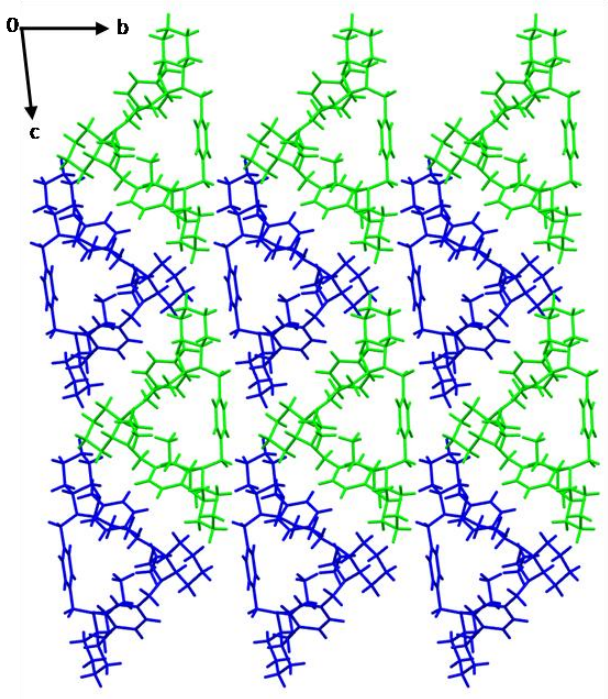


Figure S21. A packing diagram of **3b**. The two symmetry independent host molecules are shown in green and blue in sticks style.

Table S5. Selected torsion angles describing the conformation of macrocycle **3b**.

	Torsion angle [°]	Conformation
N1-C1-C2-N2	-42.2(6)	*G*$^-$
C1-C2-N2-C10	154.7(6)	*T*
C2-N2-C10-C11	173.5(6)	*T*
C14-C17-N3-C18	-170.6(6)	*T*
C17-N3-C18-C19	-91.0(6)	*A* (anticlinal)
N3-C18-C19-N4	-39.3(6)	*G*$^-$
C18-C19-N4-C27	149.0(5)	*T*
C19-N4-C27-C28	170.9(5)	*T*
C31-C34-N5-C35	-168.0(5)	*T*
C34-N5-C35-C36	-83.4(7)	*A* (anticlinal)
N5-C35-C36-N6	-41.2(7)	*G*$^-$
C35-C36-N6-C44	151.5(6)	*T*
C36-N6-C44-C45	175.8(6)	*T*
C48-C51-N1-C1	-168.2(5)	*T*
C51-N1-C1-C2	-84.5(6)	*A* (anticlinal)
N7-C52-C53-N8	-37.8(7)	*G*$^-$

C52-C53-N8-C61	-84.1(7)	*A* (anticlinal)
C53-N8-C61-C62	-168.6(6)	*T*
C65-C68-N9-C69	170.7(6)	*T*
C68-N9-C69-C70	156.3(6)	*T*
N9-C69-C70-N10	-43.8(6)	G^-
C69-C70-N10-C78	-84.0(6)	*A* (anticlinal)
C70-N10-C78-C79	-173.6(6)	*T*
C82-C85-N11-C86	174.6(6)	*T*
C85-N11-C86-C87	152.1(6)	*T*
N11-C86-C87-N12	-41.8(7)	G^-
C86-C87-N12-C95	-82.9(7)	*A* (anticlinal)
C87-N12-C95-C96	-165.4(6)	*T*
C99-C102-N7-C52	174.1(5)	*T*
C102-N7-C52-C53	146.4(6)	*T*

Crystal 3c

Crystals of **3c** were obtained from slow evaporation of a *m*-xylene at room temperature. The asymmetric unit, shown in Fig. S22 contains one symmetry independent molecule of **3c** and one molecule of *m*-xylene. Host-guest ratio is 1:1.

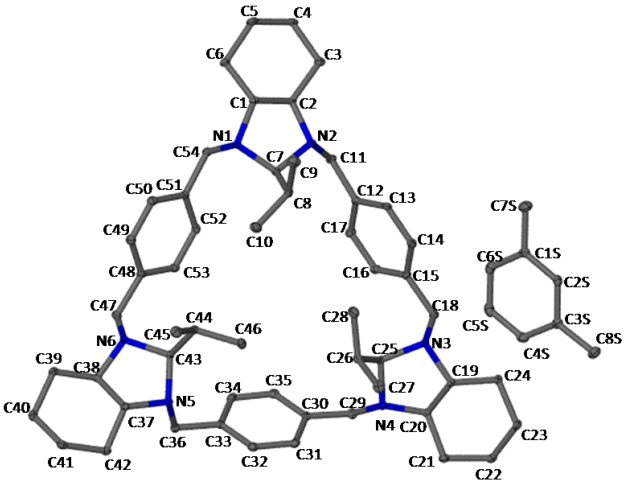


Figure S22. Asymmetric unit of **3c** together with labeling scheme. Ellipsoids are drawn at the 30% probability level. Hydrogen atoms have been omitted for clarity.

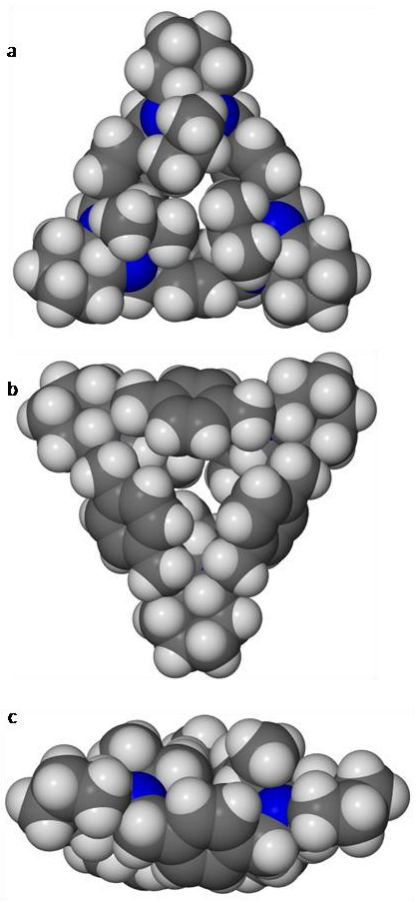


Figure S23. Molecular shape of **3c** illustrated in space-filling mode. Figures a, b and c represent a top, bottom and a side view of macrocycle, respectively.

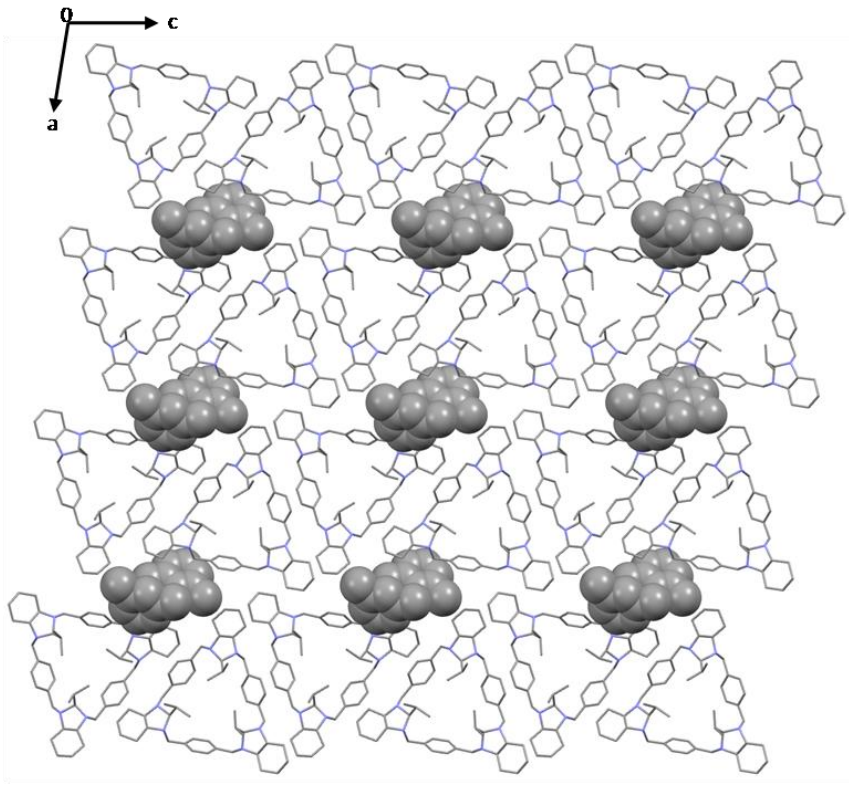


Figure S24. A packing diagram of **3c** as viewed along the *b* lattice direction. Host molecules have been illustrated in capped sticks mode whereas guest molecules are shown as space-filling model. All H atoms are omitted for clarity.

Table S6. Selected torsion angles describing the conformation of macrocycle **3c**.

	Torsion angle [°]	Conformation
N1-C1-C2-N2	-40.2(2)	*G*$^-$
C1-C2-N2-C11	149.6(2)	*T*
C2-N2-C11-C12	175.3(2)	*T*
C15-C18-N3-C19	178.2(2)	*T*
C18-N3-C19-C20	-83.8(3)	*A* (anticlinal)
N3-C19-C20-N4	-40.1(2)	*G*$^-$
C19-C20-N4-C29	152.4(2)	*T*
C20-N4-C29-C30	166.6(2)	*T*
C33-C36-N5-C37	-176.2(2)	*T*
C36-N5-C37-C38	-79.4(2)	*G*$^-$
N5-C37-C38-N6	-43.1(2)	*G*$^-$
C37-C38-N6-C47	152.6(2)	*T*
C38-N6-C47-C48	174.5(2)	*T*
C51-C54-N1-C1	-171.5(2)	*T*
C54-N1-C1-C2	-82.9(2)	*A*

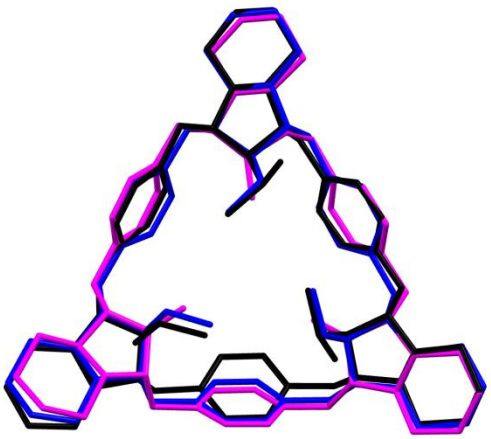


Figure S25. An overlay of the molecules **3a** (magenta), **3b** (blue) and **3c** (black).

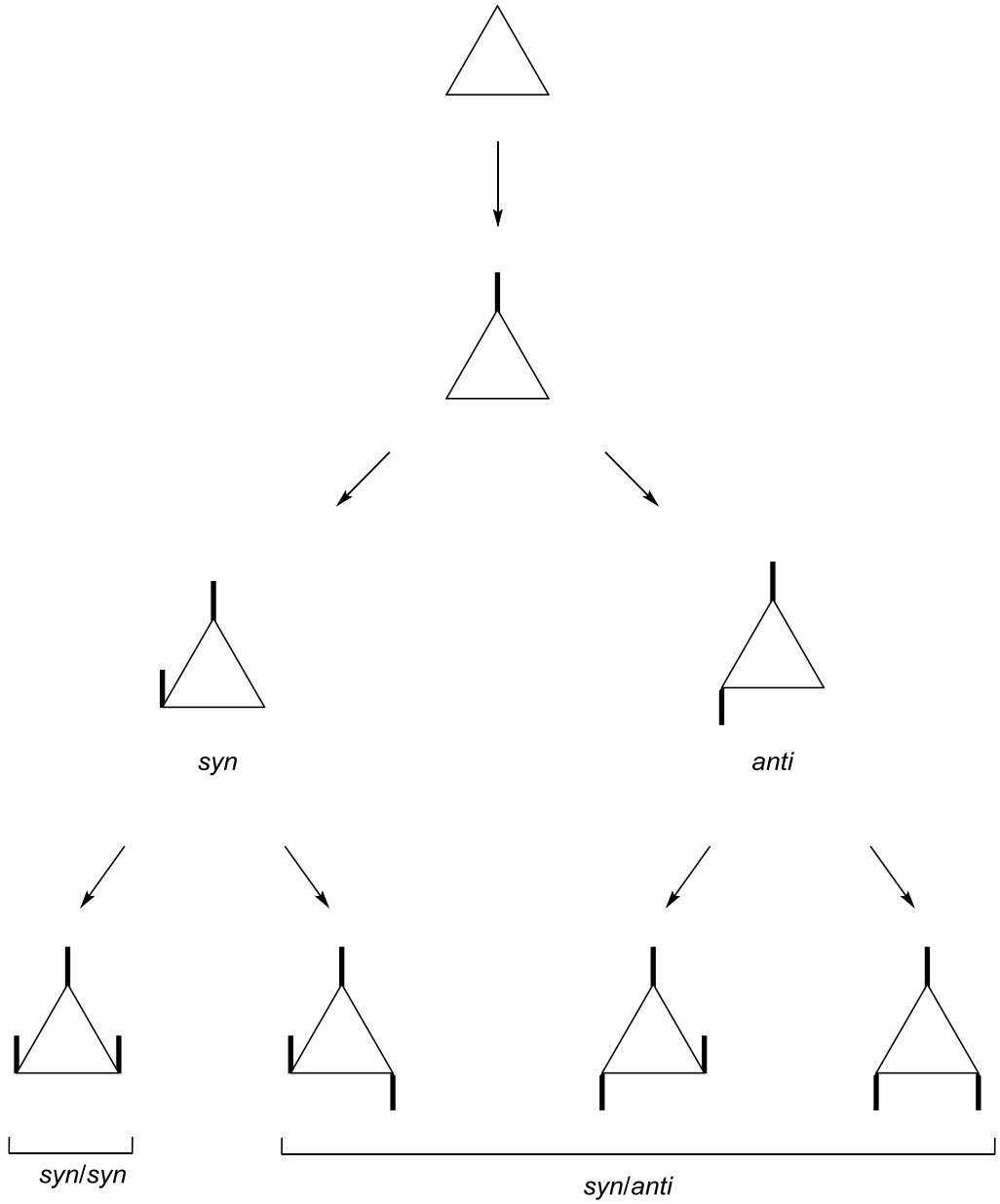


Figure S26. Stepwise derivatization scheme.

Calculation details and atomic coordinates for low energy conformers of **3b**

Preliminary conformer distribution search was performed by the Scigress package[9] using the MM3 molecular mechanics force field. All possible conformers were analyzed using the systematic search methodology. Minimum energy conformers of relative steric energies (ΔE_{SE}) up to 10 kcal mol^{-1} found by molecular mechanics were further fully optimized using PM6 semiempirical method level and then at the B3LYP/6-311G(d,p) level as implemented in the Gaussian09 package,[10] The conformers obtained at the B3LYP/6-311G(d,p) level were the real minima (no imaginary frequencies have been found). CD spectrum calculation for lowest energy conformer was performed at cam-b3lyp/6-311g(d,p)) using Gaussian09 package.

Atomic coordinates for low energy structures of **3b**

Conformation syn/syn

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Conformation syn/anti

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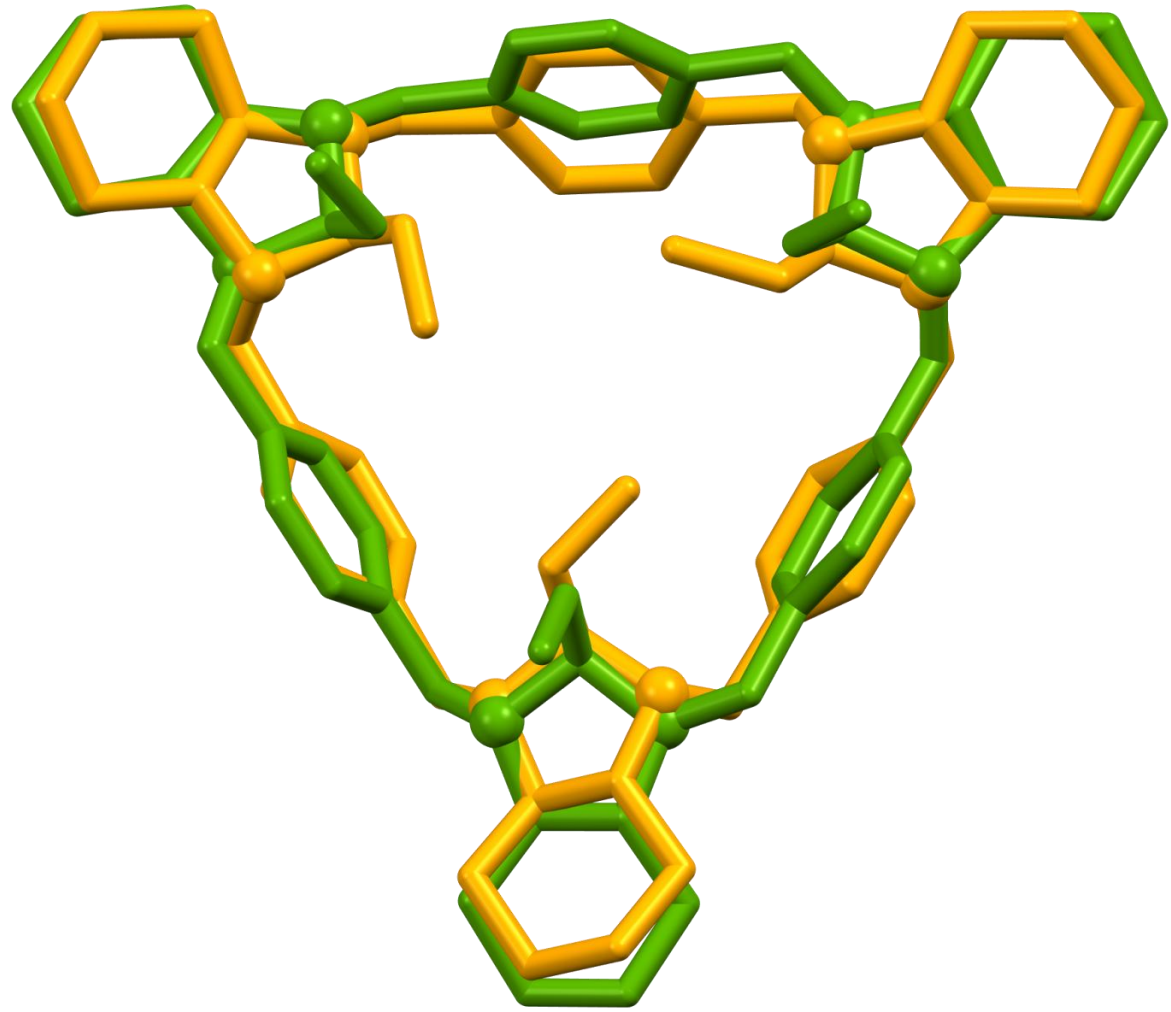
H	0.60993386	1.94072922	-5.25280480
H	5.40750271	-6.19631933	-1.90089261
H	4.19968844	-7.51628923	-6.52724921
H	2.98758704	-3.49595485	0.96645399
H	6.55742936	-2.60363221	-2.33664729
H	-0.47172427	-5.66046620	-4.52435634
H	3.06064245	-5.67407222	-7.97828991
H	-1.85012285	-5.06430937	-7.49078363
H	-2.68215116	-0.58062855	-4.20126946
H	1.09271870	2.31796096	-2.86431409
H	-0.52263328	0.80790970	-6.96192635
C	4.78384965	-5.00850857	-4.32465572
C	4.38456710	-3.55832861	-4.64151219
C	5.36745474	-2.81029184	-5.54221411
C	-0.75366311	-2.00376234	-6.53196151
H	3.99003288	-5.44677003	-3.70018983
H	3.40395021	-3.60098065	-5.12519800
H	4.24795166	-3.01725428	-3.70272020
H	5.02359069	-1.78822575	-5.72384264
H	6.35881313	-2.75886358	-5.08597684
H	5.46013221	-3.30926812	-6.51004855

C	0.71552446	-1.62774081	-6.82261964
C	1.05581070	-1.24462863	-8.26564167
H	1.00608042	-0.82449760	-6.13772644
H	1.31872861	-2.49247648	-6.53368733
H	2.13426166	-1.09928784	-8.37563773
H	0.74746427	-2.03086494	-8.95726601
H	0.56871776	-0.31691569	-8.57754243
H	-0.78973101	-2.34041300	-5.48511865
H	3.75393671	0.12031950	0.19843670
H	0.65121626	1.96739745	-0.59198137
C	0.06869193	-2.99993421	-0.41580953
H	1.88813765	-2.46701762	-1.45939091
H	0.44503234	-1.70630256	-2.09967894
H	-0.90037298	-2.55736397	-0.17267612
H	0.54233360	-3.31512237	0.51651362
H	-0.11026701	-3.89166215	-1.02298878

(a)



(b)

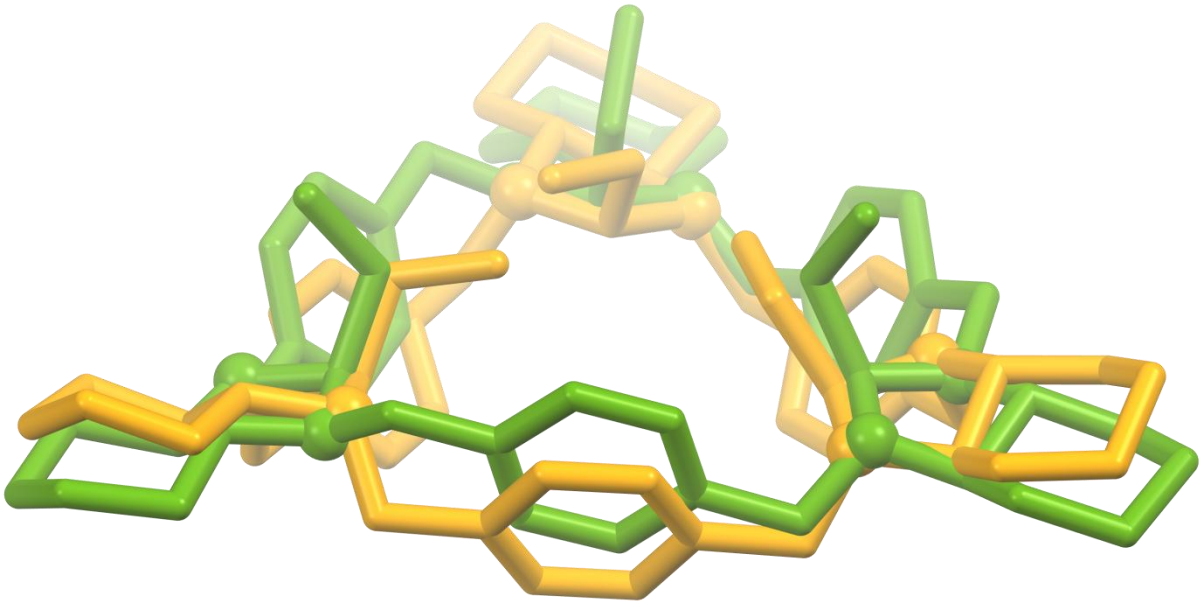


Figure S27 An overlay of experimental (X-ray, yellow) and calculated (DFT, green) molecules **3b** showing differences in their conformation: a top (a) and side (b) view.

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