- Supporting Information –

A lipophilic "fully-*anti*" dodecamer from mutagenic (5'*S*)-5',8-cyclo-2'-deoxyguanosine

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A. Materials and methods.

Derivative **1** was prepared as reported in Terzidis, M. A.; Chatgilialoglu, C. *Aust. J. Chem.* **2013**, *66*, 330. Chemicals were purchased from Aldrich Chemical Co. (Aldrich or Fluka catalogues) and used without further purification.

CD spectra were recorded on a JASCO J-715 Spectropolarimeter (path length = 0.01 cm).

NMR spectra were recorded on a Varian Inova (600 MHz) instrument equipped with either a direct or a reverse probe.

SANS experiments were performed at the D11 instrument (ILL, Grenoble, France). The used neutron wavelenght λ was 6 Å and two sample-detector distances (8 and 1.2 m) were used in order to cover a Q-range ($Q = (4\pi \sin\theta)/\lambda$, where 2θ is the scattering angle) from 0.01 to 0.5 $Å^{-1}$. Samples were measured at different temperatures in a 1 mm thick quartz cell. Raw data, obtained at different sample-to-detector distances, have been radially averaged, calibrated using transmission values and detector efficiency and transformed in absolute units (cm^{-1}). Moreover, the $CDCl_3$ contribution corrected for the **1** volume fraction has been subtracted from the solution signal. The SANS curves report macroscopic differential scattering cross sections, $I(Q)$, measured as a function of the modulus of the momentum transfer. Fitting parameters are: Rc = 7.8 ± 0.9 Å, t=4.5 ± 0.8 Å, L = 12.6 ± 1.5 Å, SLD_{core} = 4.34 10^{-6} $Å^{-2}$ and SLD_{shell} = 2.02 10^{-6} $Å^{-2}$ at 5°C; Rc = 7.7 ± 1.0 Å, t = 4.1 ± 0.8 Å, L = 12.7 ± 1.3 Å, SLD_{core} = 4.30 10^{-6} $Å^{-2}$ and SLD_{shell} = 2.01 10^{-6} $Å^{-2}$ at 25°C; Rc = 8.7 ± 1.1 Å, t=4.1 ± 0.5 Å, L = 11.8 ± 1.5 Å, SLD_{core} = 4.29 10^{-6} $Å^{-2}$ and SLD_{shell} = 2.02 10^{-6} $Å^{-2}$ at 50°C.

1-SrP_2 solutions. $CDCl_3$ solutions containing the dodecameric complex (**1**-SrP_2 solutions) were prepared by solid-liquid extraction: 1 mL of **1** solution (8, 30 or 50 mM) was stirred with one equivalent (unless otherwise specified) of solid strontium picrate for four days at room temperature. The organic phase was then separated from the excess of solid salt by centrifugation, and used for CD, NMR or SANS investigations.
In titration experiments with cryptand [2.2.2], a **1**-SrP_2 $CDCl_3$ solution ([**1**] = 8 mM) was added with increasing amounts of solid cryptand. Subsequent titration with trifluoromethanesulfonic acid (Thf) was carried out by adding increasing amounts of a 35 mM $CDCl_3$ solution of the acid.

B. CD measurements

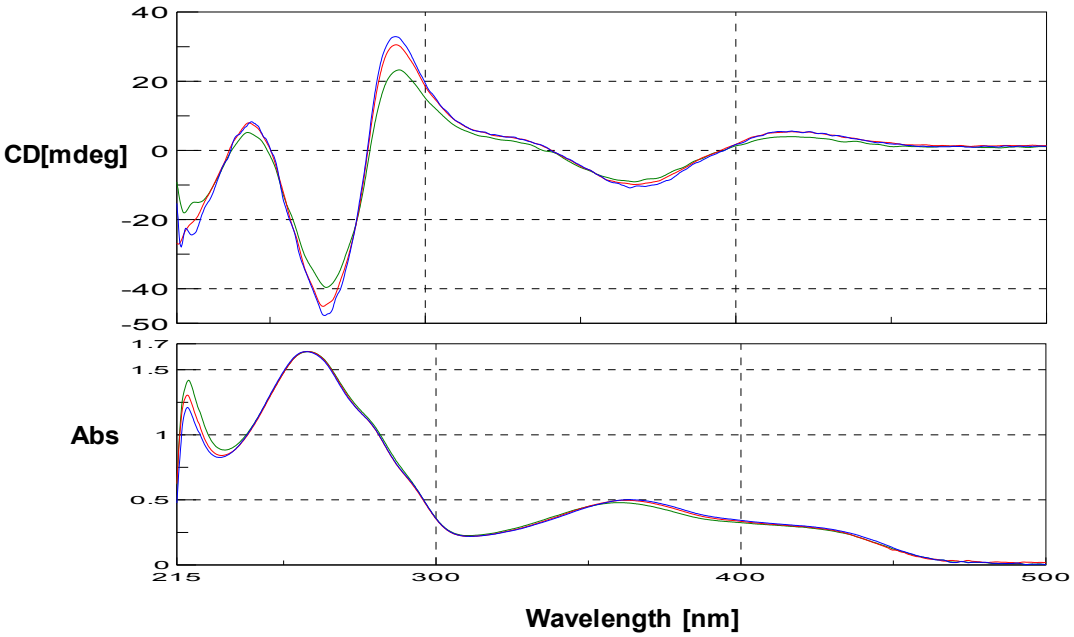


Figure S1. CD/UV spectra recorded at different temperatures on a $CDCl_3$ solution of **1** (8 mM) after extraction of 1/6 eq. of SrP_2. Blue trace: 5°C; Red trace: 25°C; Green trace: 40°C.

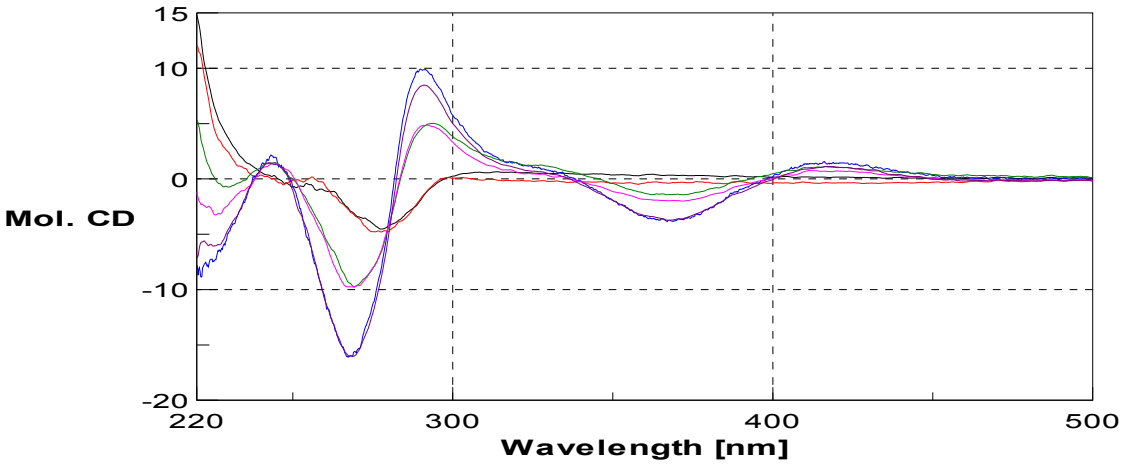


Figure S2. CD spectra recorded in $CDCl_3$ at 25°C. Black trace: **1** 8 mM; blue trace (solution S_0): **1** 8 mM after solid-liquid extraction of 1/6 eq. of SrP_2; Pink trace: solution S_0 added with 1/2 eq. of cryptand [2.2.2] relative to Sr^{2+}; Red trace (solution S_1): solution S_0 added with 1 eq. of cryptand [2.2.2] relative to Sr^{2+}; Green trace: solution S_1 added with ½ eq. of Htf relative to [2.2.2]; Violet trace: solution S_1 added with 1 eq. of Htf relative to [2.2.2].

C. NMR experiments

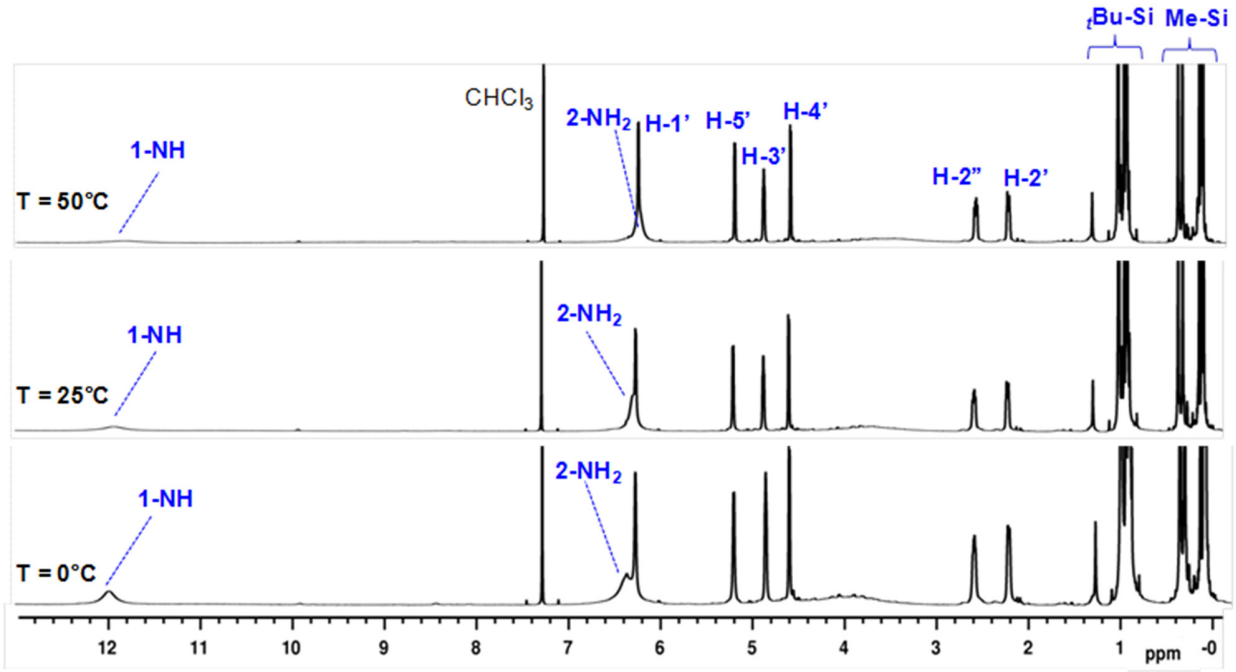


Figure S3. ^{1}H NMR spectra recorded on **1** in $CDCl_3$ (30 mM) at different temperatures. Peaks are assigned as reported in Terzidis, M. A.; Chatgilialoglu, C. *Aust. J. Chem.* **2013**, *66*, 330.

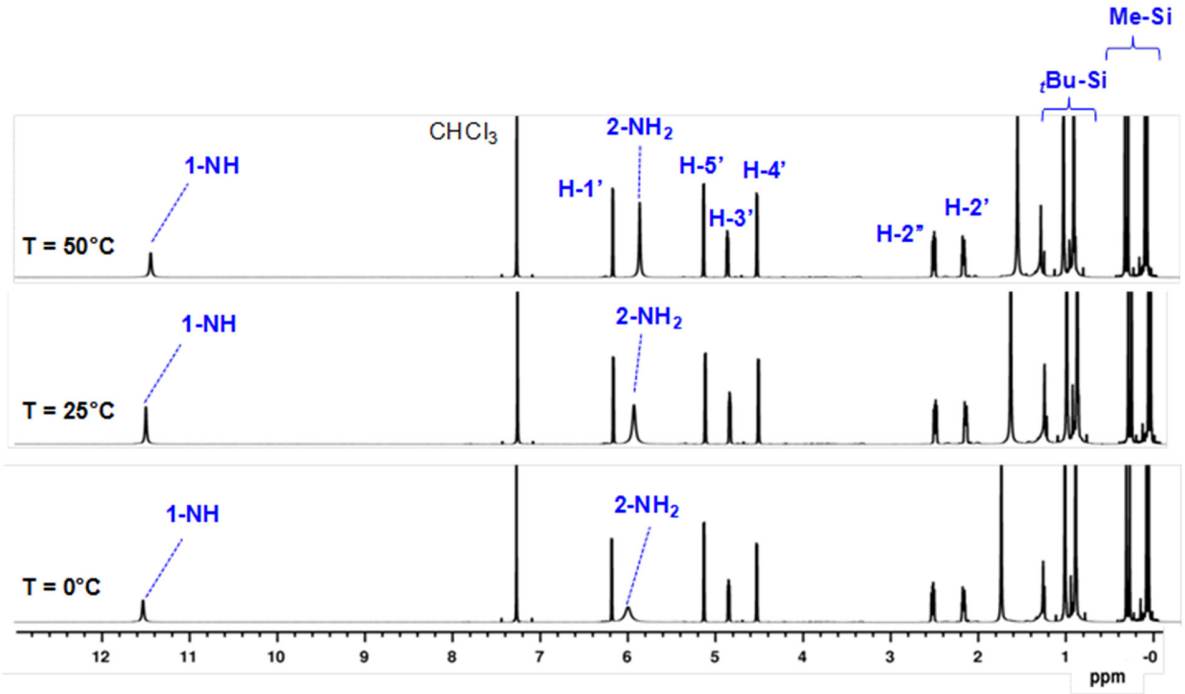


Figure S4. ^{1}H NMR spectra recorded on **1** in $CDCl_3$ (8 mM) at different temperatures. Peaks are assigned as reported in Terzidis, M. A.; Chatgilialoglu, C. *Aust. J. Chem.* **2013**, *66*, 330.

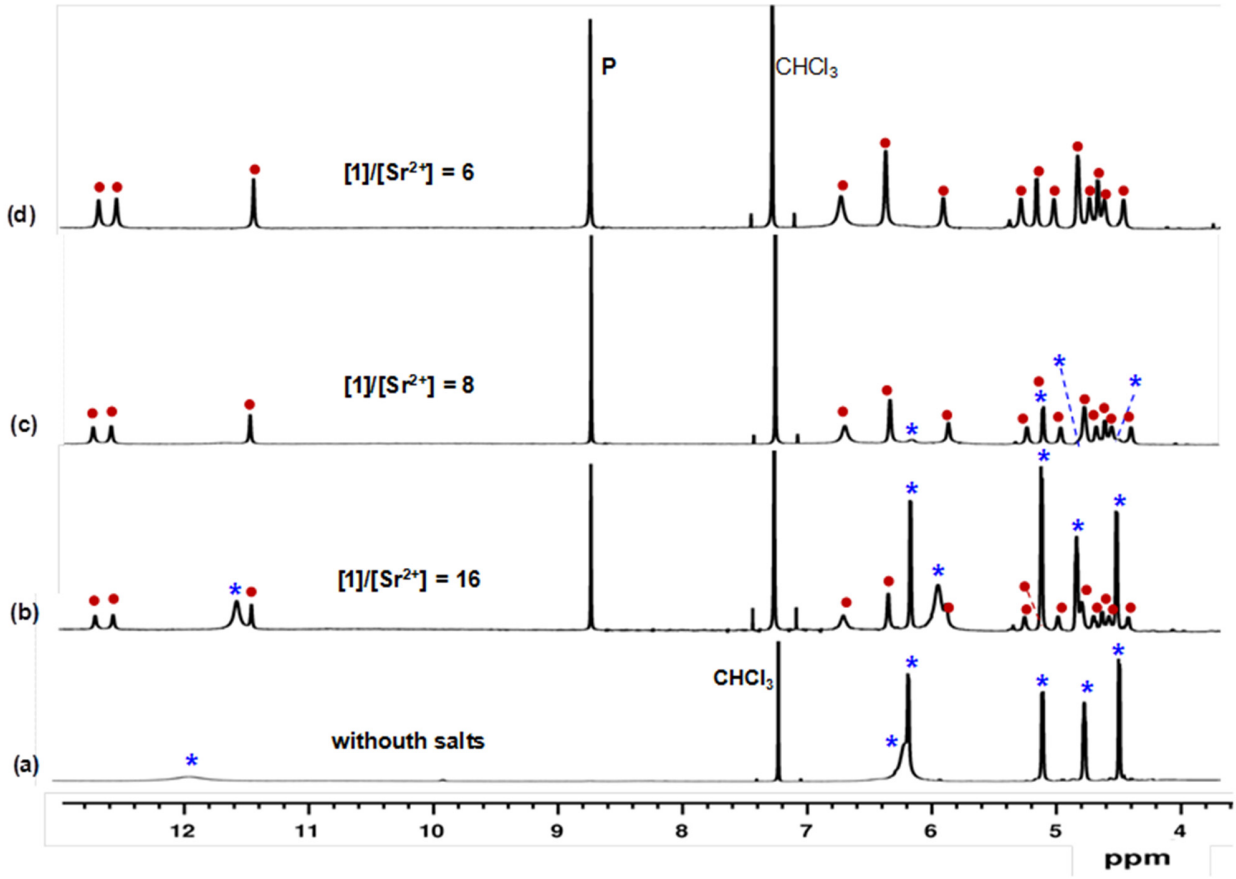


Figure S5. ^{1}H NMR spectra recorded at 25°C in $CDCl_3$. Spectrum (a): initial solution S_i containing **1** 30 mM. Spectra (b)-(d): solutions obtained from S_i by solid-liquid extraction of SrP_2, performed in the presence of (b) 1/16 eq., (c) 1/8 eq.,(d) ≥ 1/6 eq. of salt relative to **1**. Blue asterisks: **1** signals; red dots: **D** signals. The picrate anion is labeled with "P".

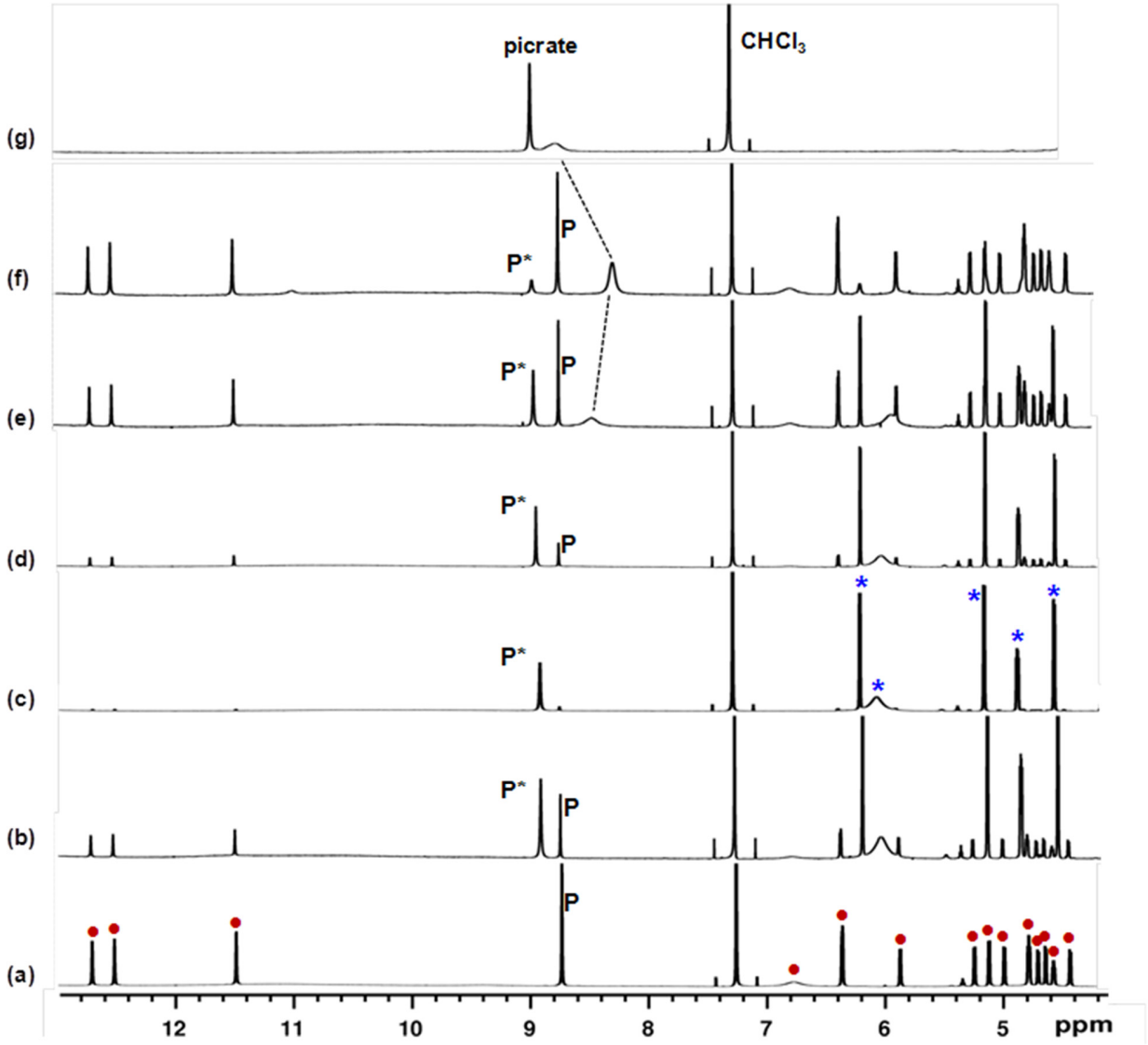


Figure S6. ^{1}H NMR spectra recorded in $CDCl_3$ at 0°C. (a) initial solution S_i, containing **1** (8 mM) and 1/6 eq. of SrP_2; (b) solution S_i added with 0.75 eq. of [2.2.2] relative to Sr^{2+}; (c) solution S_1, obtained by solution S_i added with 1 eq. of [2.2.2] relative to Sr^{2+}; (d) solution S_1 added with 0.25 eq. of Htf relative to [2.2.2]; (e) solution S_1 added with 0.5 eq. of Htf relative to [2.2.2]; (f) solution S_1 added with 1 eq. of Htf relative to [2.2.2] (from integration uncomplexed [**1**] ≤ 10%).

Red dots: **D** signals; blue asterisks: **1** signals; "P": picrate counterion of the **D** species; "P*": picrate counterion of cryptate [$Sr^{2+} \subset$ 2.2.2].

The broad resonance appearing at 8÷8.5 ppm in spectra (e) and (f) can be ascribed to protonation of cryptand [2.2.2]. See for comparison spectrum (g).

(g) $CDCl_3$ solution of cryptand [2.2.2] (1.3 mM) upon solid-liquid extraction of SrP_2 (performed with an excess of salt), and added with 0.5 eq. of Htf (relative to cryptand). Spectrum is recorded at 25°C.

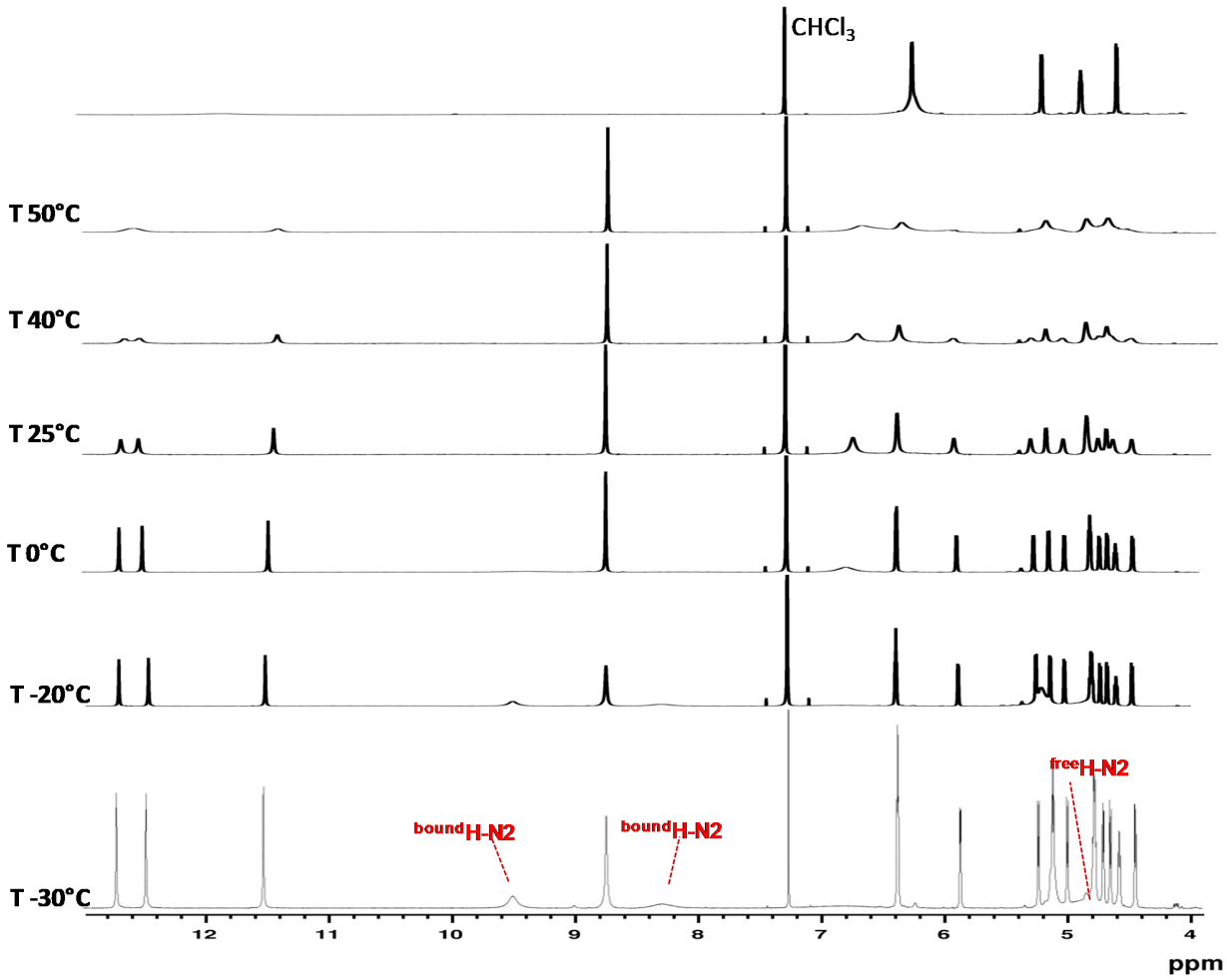


Figure S7. ^{1}H NMR experiments, recorded at different temperatures, on a 30 mM $CDCl_3$ solution of **1** after solid-liquid extraction of SrP_2 (1/6 eq. relative to **1**). In the upper part, spectrum of **1** (30 mM) is reported for comparison. For assignment of amino protons see Figure S8.

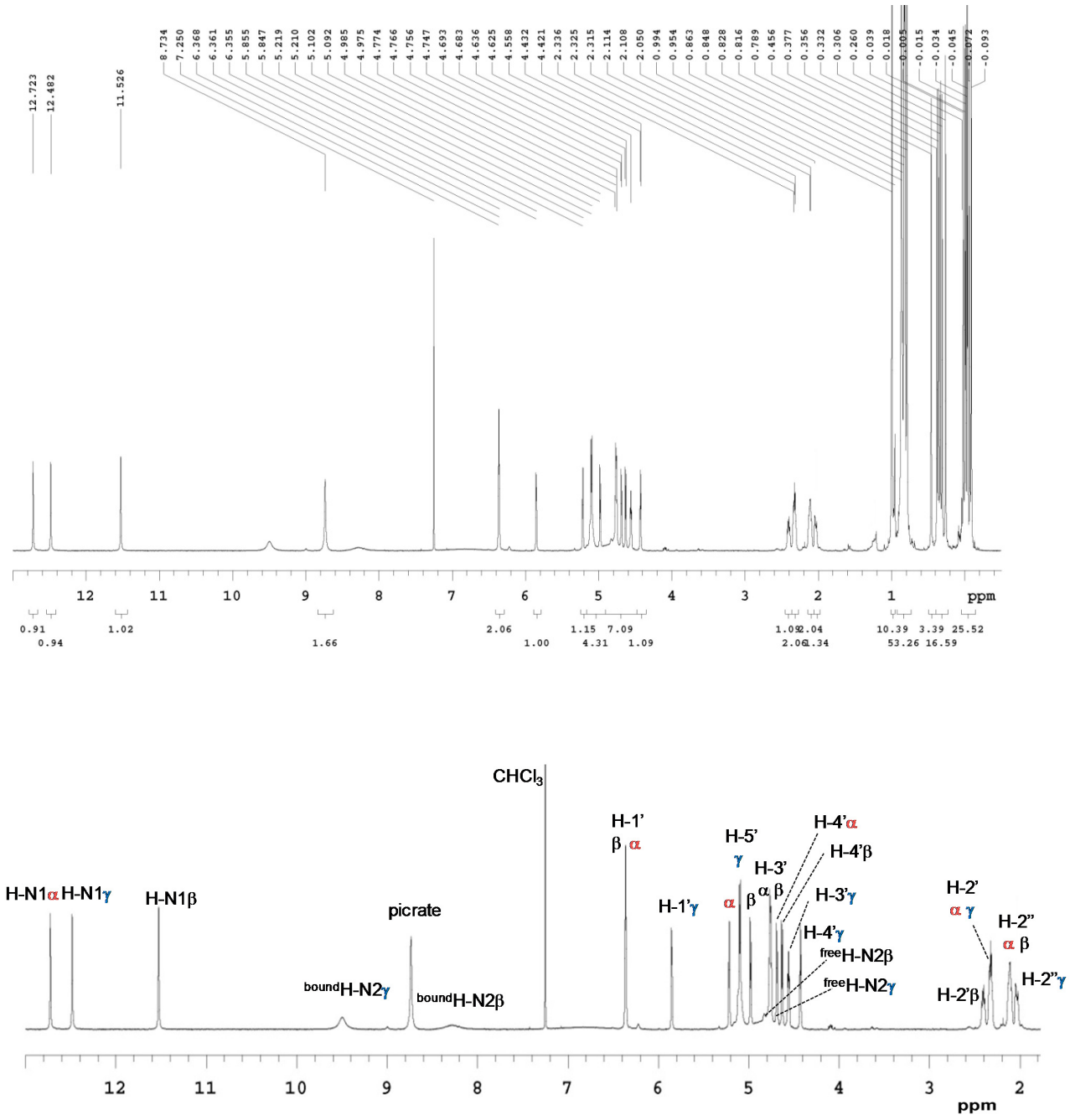


Figure S8. Top: ^{1}H NMR spectrum of **1**/SrP_2 6:1 in $CDCl_3$ at -20°C ([**1**] = 30 mM). Bottom: expansion of the 1.8-13 ppm interval of the same spectrum.

	α	β	γ
H1'	6.35	6.37	5.85
H2'	2.33	2.40	2.32
H2''	2.12	2.10	2.03
H3'	4.77	4.76	4.56
H4'	4.69	4.63	4.43
H5'	5.21	5.10	4.98
HN1	12.72	11.52	12.48
bound HN2	*	8.3	9.5
free HN2	*	4.9	4.8
C2	153.91	153.77	152.78 n.a.
C4	149.75	148.32	147.12 n.a.
C5	115.07	115.86	114.28
C6	159.53	157.02	159.17
C8	144.24	143.01	144.65
C1'	84.70	84.51	84.51
C2'	45.18	45.52	45.85
C3'	69.35	69.16	69.07
C4'	86.63	86.71	86.27
C5'	65.81	65.19	65.15

* protons are supposed to be exchanged-broadened into the baseline

n.a. = not assigned

Table S1. ^{1}H and ^{13}C chemical shifts for **D** signals (relative to residual $CHCl_3$ – 7.25 and 77.0 ppm, respectively).

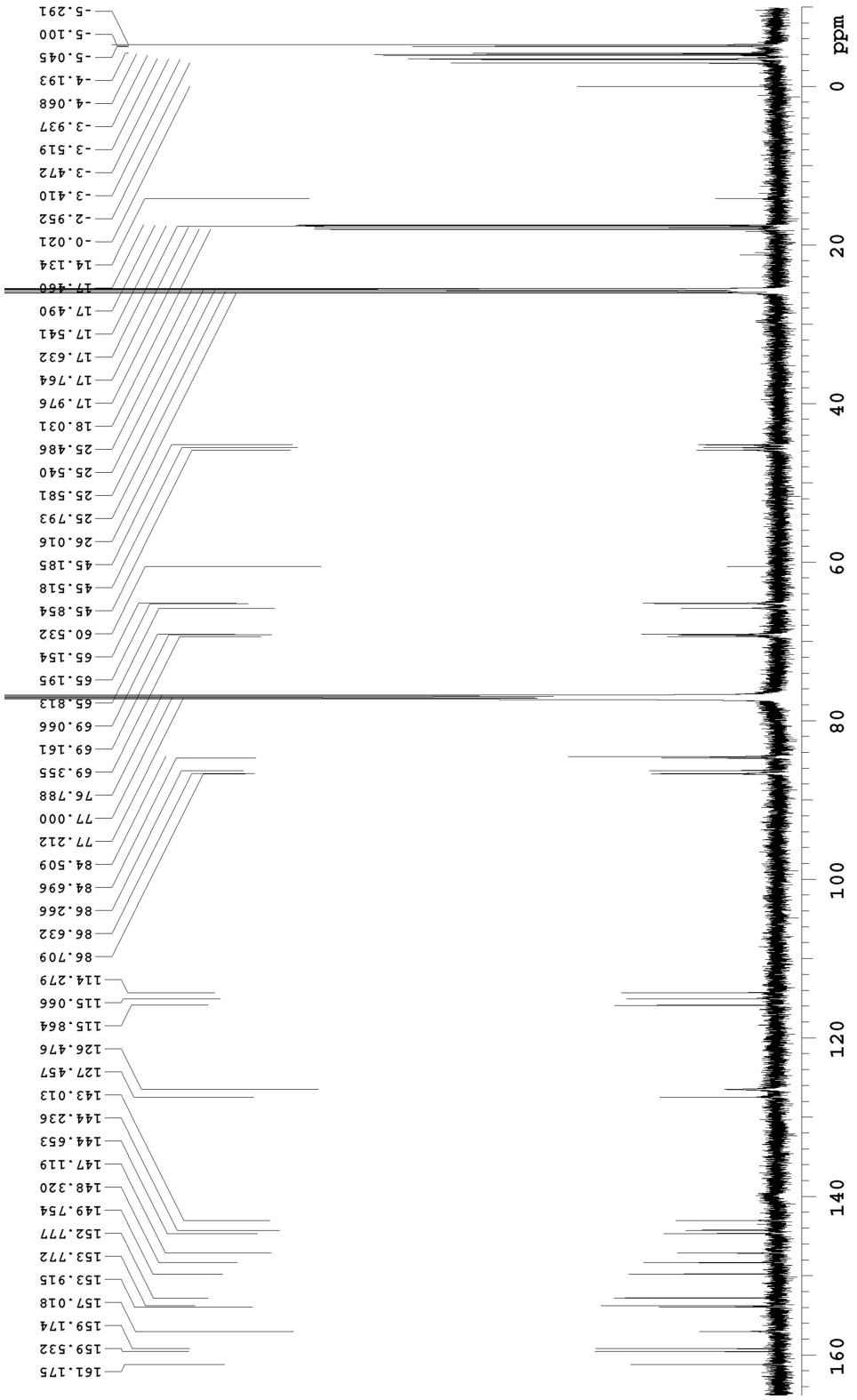
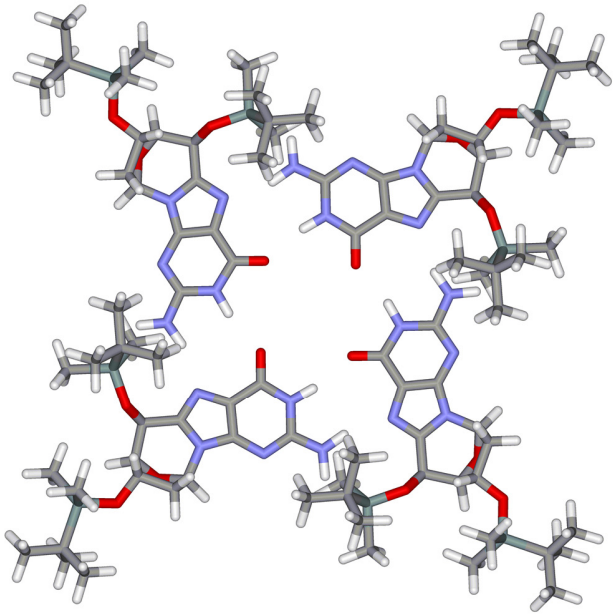


Figure S9. ^{13}C NMR spectrum of **1**/SrP_2 6:1 in $CDCl_3$ at -19°C ([**1**] = 30 mM).

a)



b)

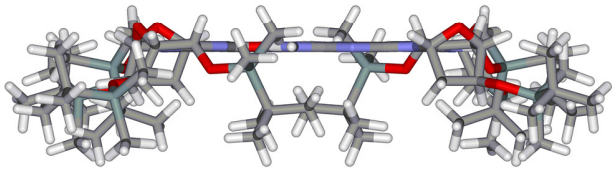
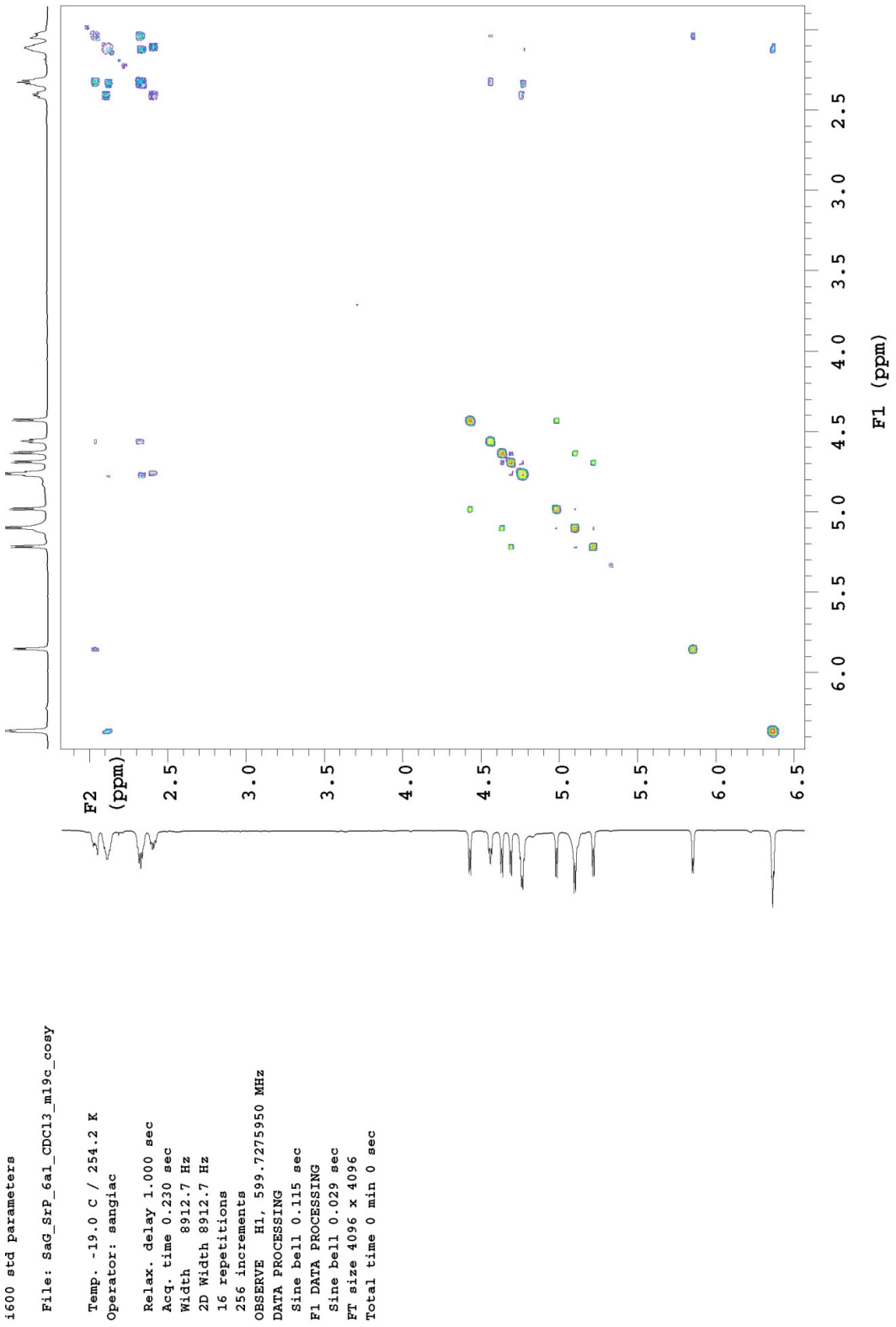


Figure S10. **a**) Top view of a G-quartet formed by **1**, seen from the *tail* face. **b**) Side view of the same quartet.

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i600 std parameters

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Temp. -19.0 C / 254.2 K
Operator: sangiac

Relax. delay 1.000 sec
Acq. time 0.230 sec
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2D Width 8912.7 Hz
16 repetitions
256 increments
OBSERVE   H1, 599.7275950 MHz
DATA PROCESSING
Sine bell 0.115 sec
F1 DATA PROCESSING
Sine bell 0.029 sec
FT size 4096 x 4096
Total time 0 min 0 sec
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Figure S11. Sugars region of the gCOSY spectrum of **1**/SrP_2 6:1 in $CDCl_3$ at -19°C ([**1**] = 30 mM).

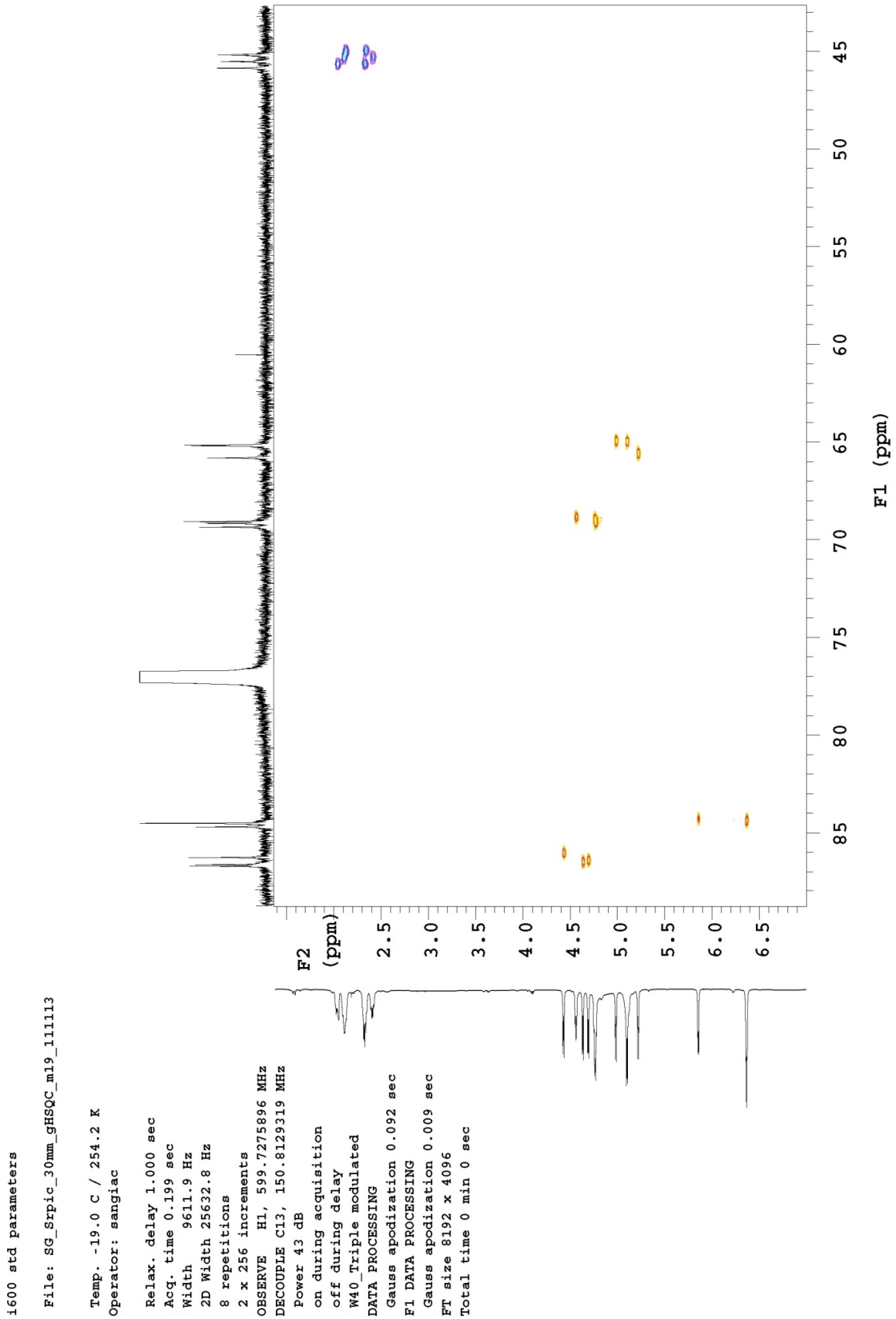

Figure S12. Sugars region of the gHSQC spectrum of **1**/SrP 6:1 in $CDCl_3$ at -19°C ([**1**] = 30 mM).

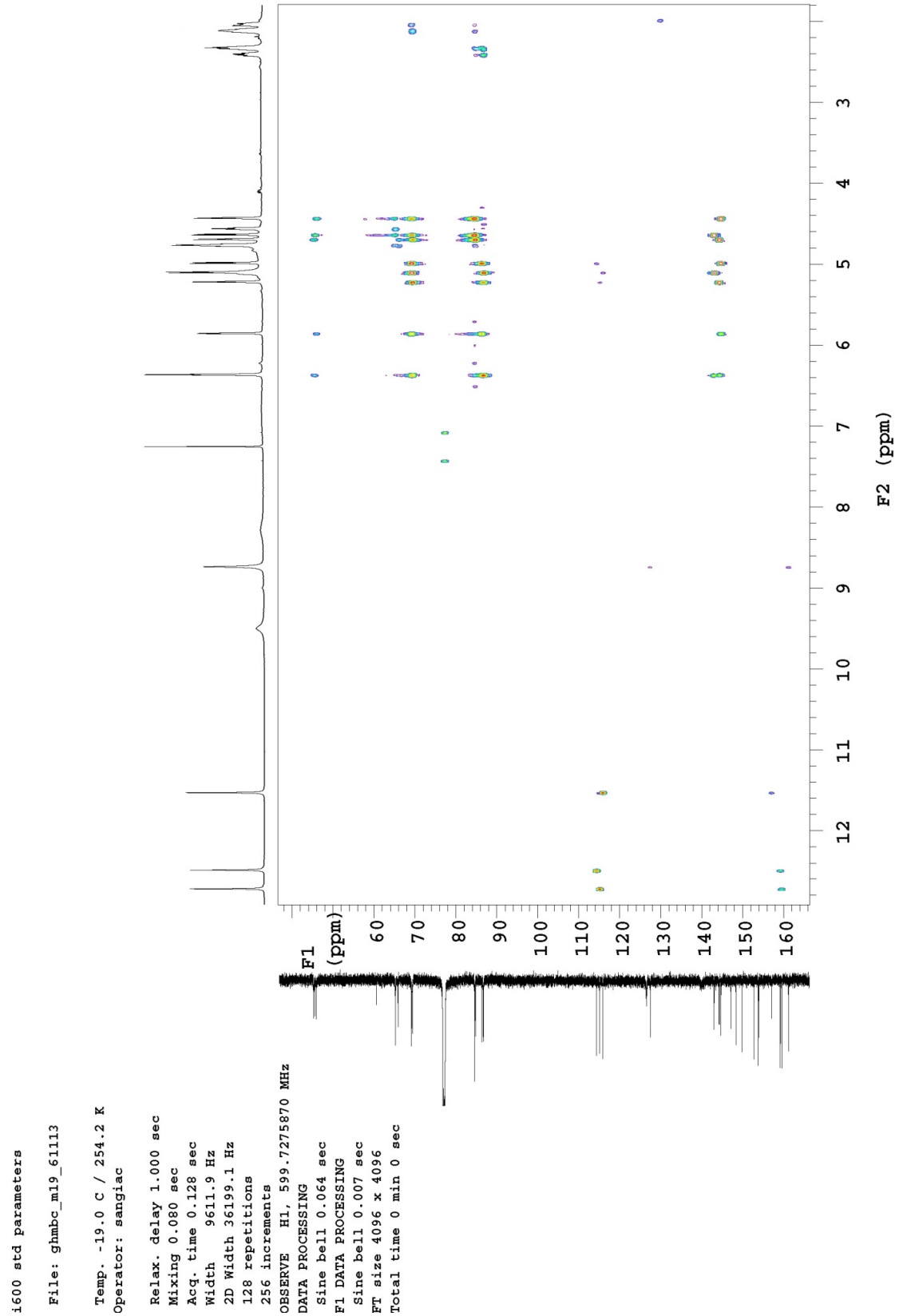

Figure S13. Sugars region of the gHMBC spectrum of **1**/SrP 6:1 in $CDCl_3$ at -19°C ([**1**] = 30 mM).

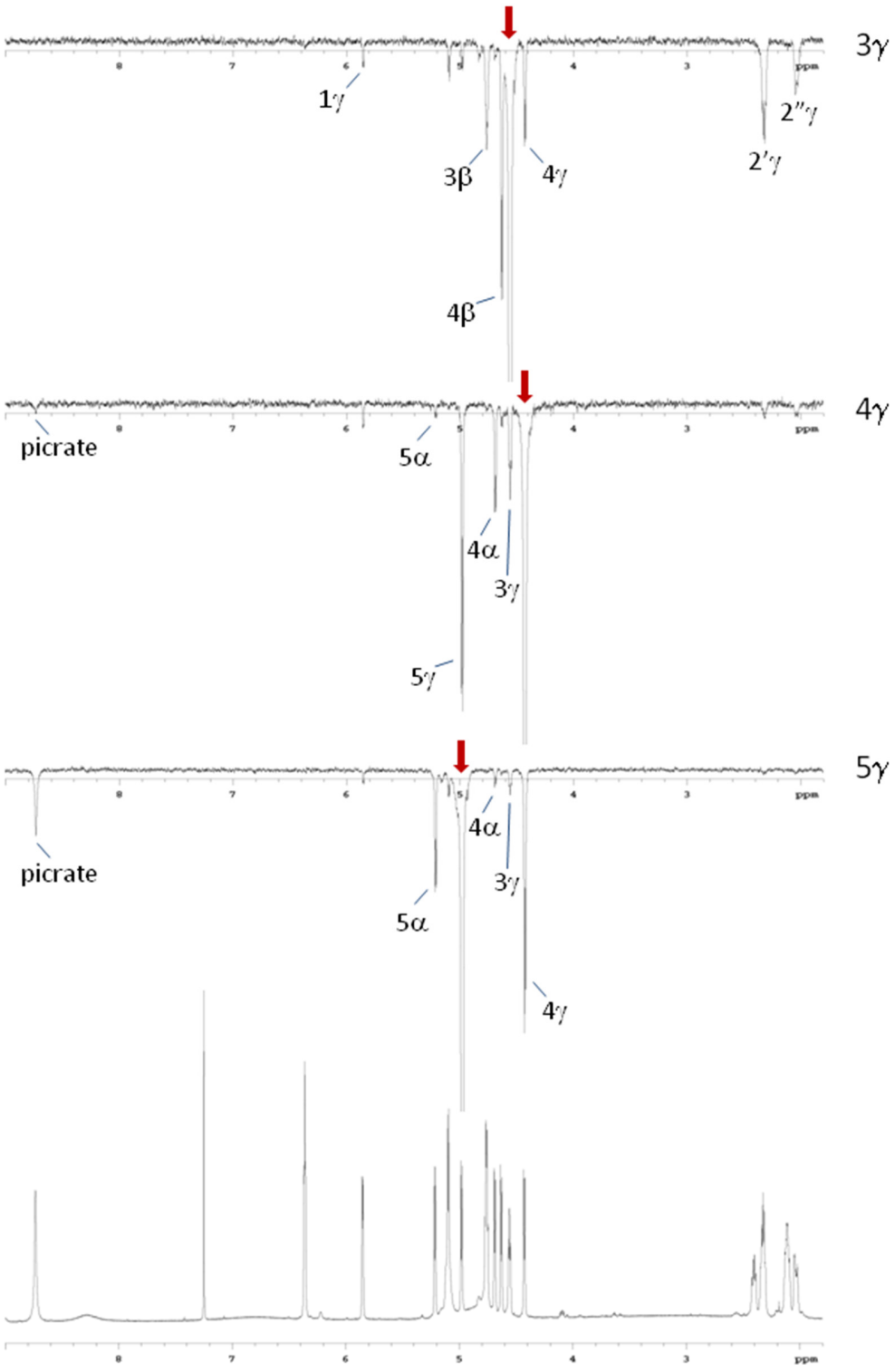

Figure S14. Noesy1d spectra recorded at -19°C on **1**/SrP 6:1 in $CDCl_3$ ([**1**] = 30 mM). Mixing time 300 ms, 256 scans, a shaped (50 Hz) pulse centered at the peak of interest was used for resonance selection.

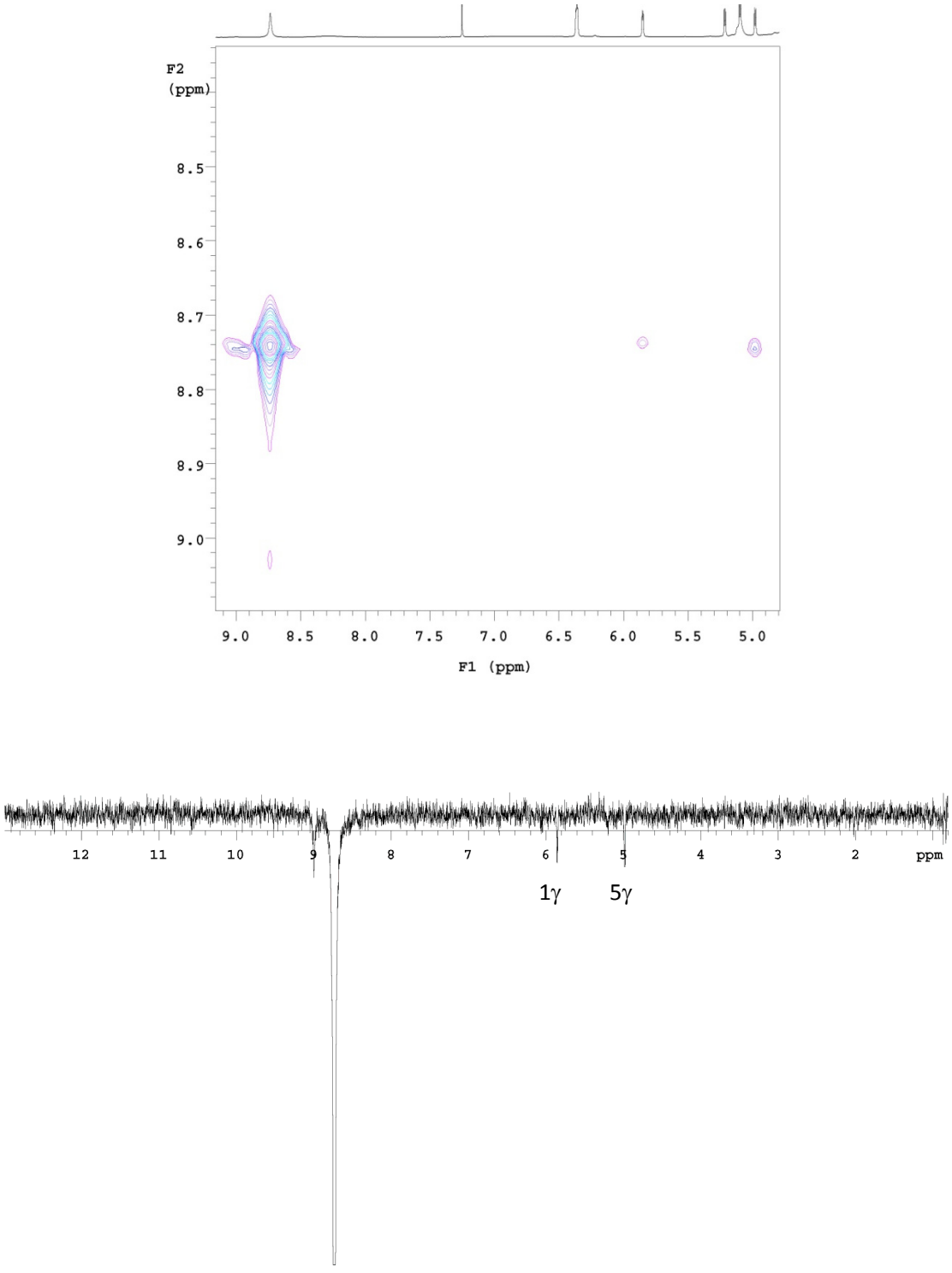

Figure S15. Portion of the 2D-noesy (top) and 1D-noesy spectra showing contacts between picrate protons and H1'γ / 5'γ.