Electronic Supplementary Information

Restricted rotation and tunable fluorescence in atropisomeric naphthyl pyridine chromophores

Olga Yunyaeva,[a] Duane Hean,[a] Michael O. Wolf[a]*

[a]Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, Canada V6T 1Z1

Table of Contents

Synthetic Schemes

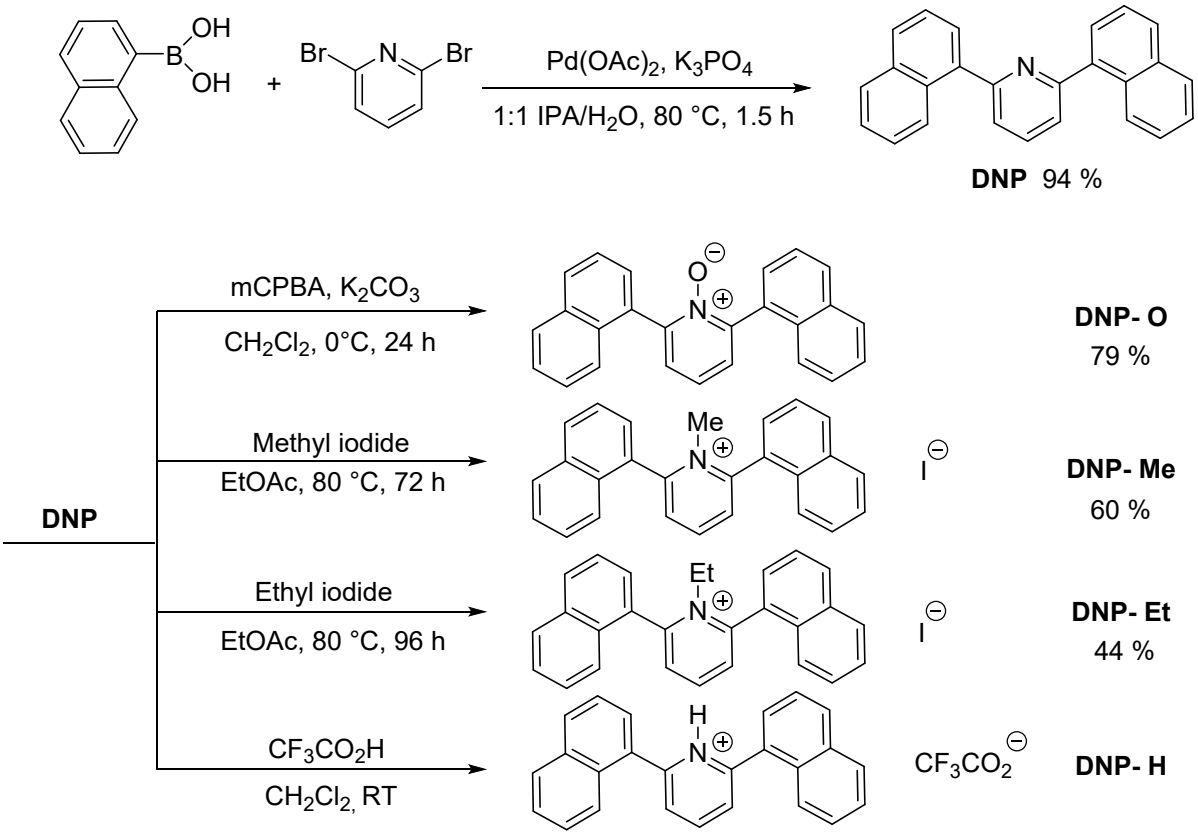

Figure S1. Synthetic route to disubstituted parent compound DNP and N-functionalized derivatives.

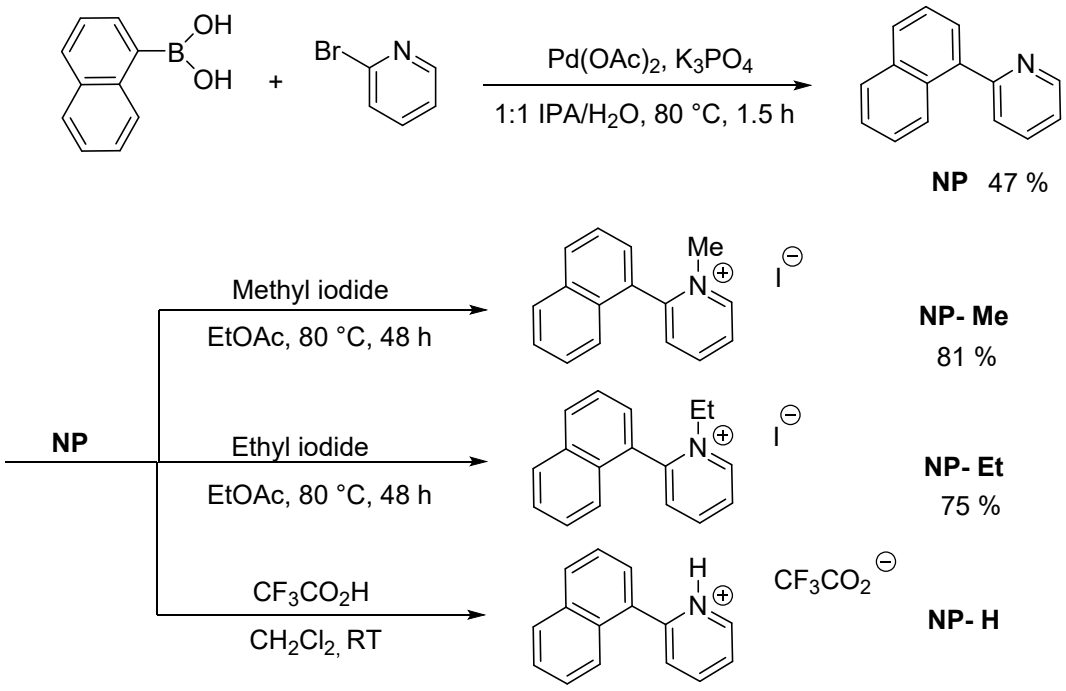

Figure S2. Synthetic route to monosubstituted parent compound NP and N-functionalized derivatives.

Additional Figures

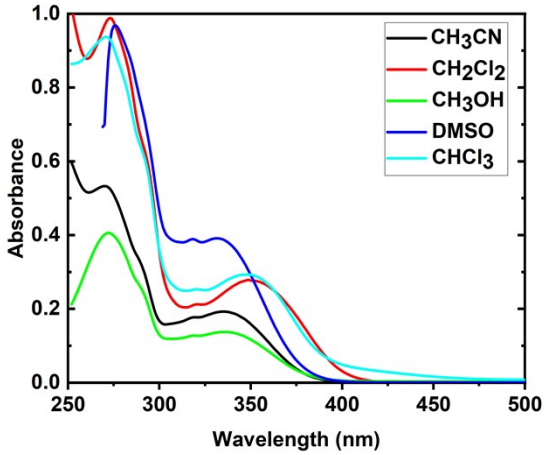

Figure S3. Absorption spectrum of **DNP-Me** in a range of solvents.

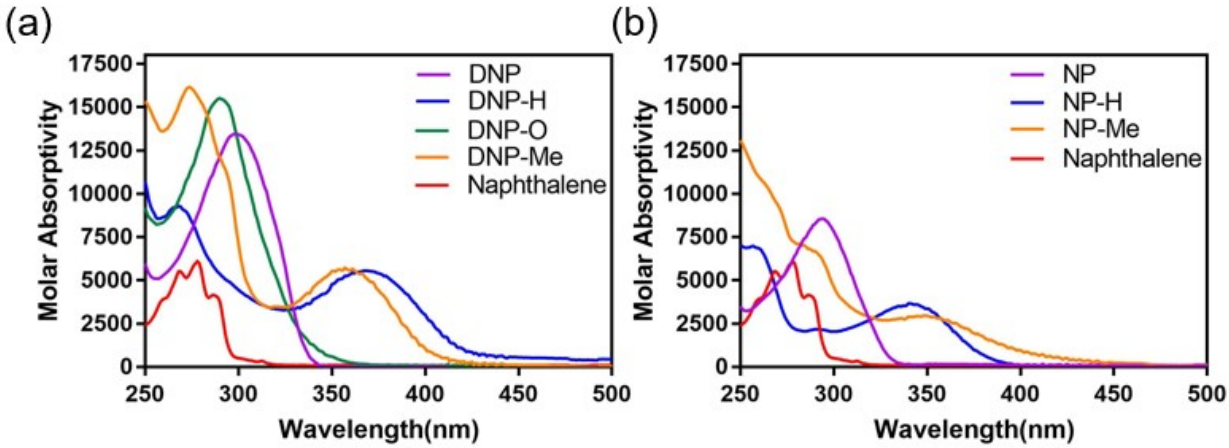

Figure S4. Molar absorptivity of (a) **DNP** and (b) **NP** compounds compared with naphthalene in CH_2Cl_2.

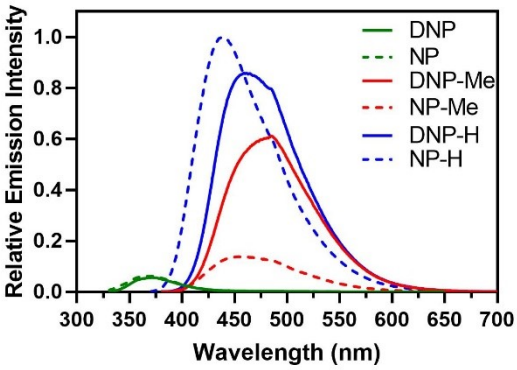

Figure S5. Relative emission spectra of **DNP** (solid line) and **NP** (dashed line) compounds taken in CH_2Cl_2 collected at an absorbance of 0.1, excited at λ_{max}.

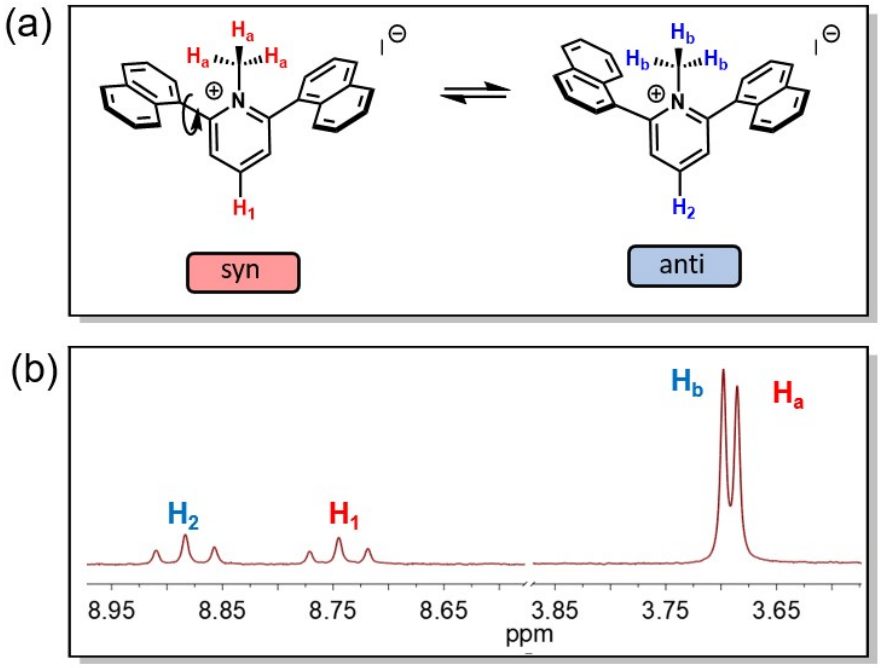

Figure S6. (a) Proposed conformations of two **DNP-Me** atropisomers (b) Portions of the ^1H NMR spectrum of **DNP-Me** in CD_2Cl_2 (400 MHz) at 25 °C.

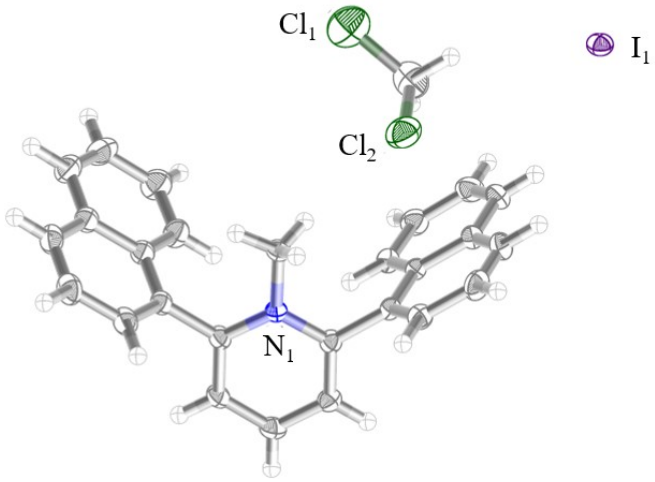

Figure S7. Crystal structure of **Me-DNP** with I- as the counterion solvated with CH_2Cl_2. Ellipsoids are plotted at the 50% probability level.

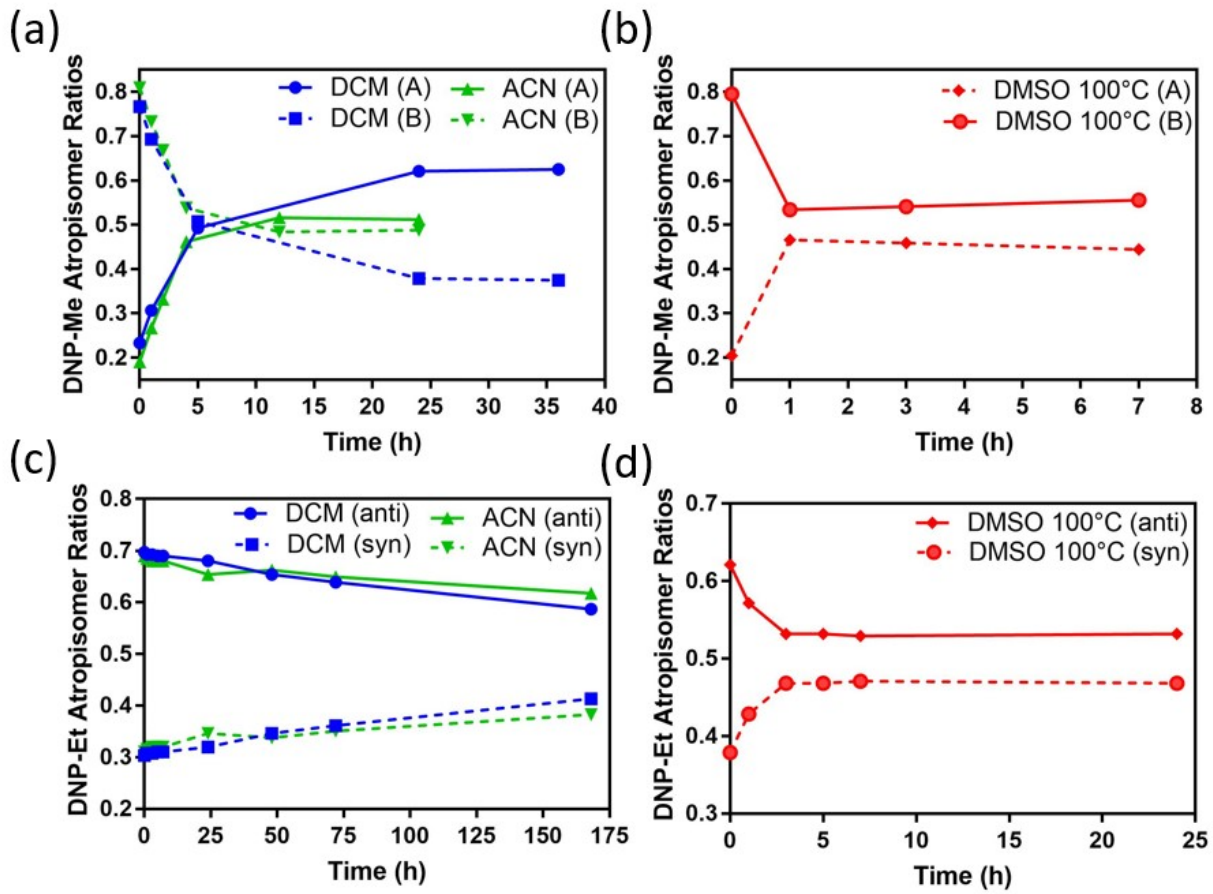

Figure S8. (a) Atropisomer ratios of **DNP-Me** over time in ambient light in $CH_2Cl_2$and CH_3CN (b) and in DMSO at 100°C. (c) Atropisomer ratios of **DNP-Et** over time in ambient light in CH_2Cl_2 and CH_3CN (d) and in DMSO at 100°C.

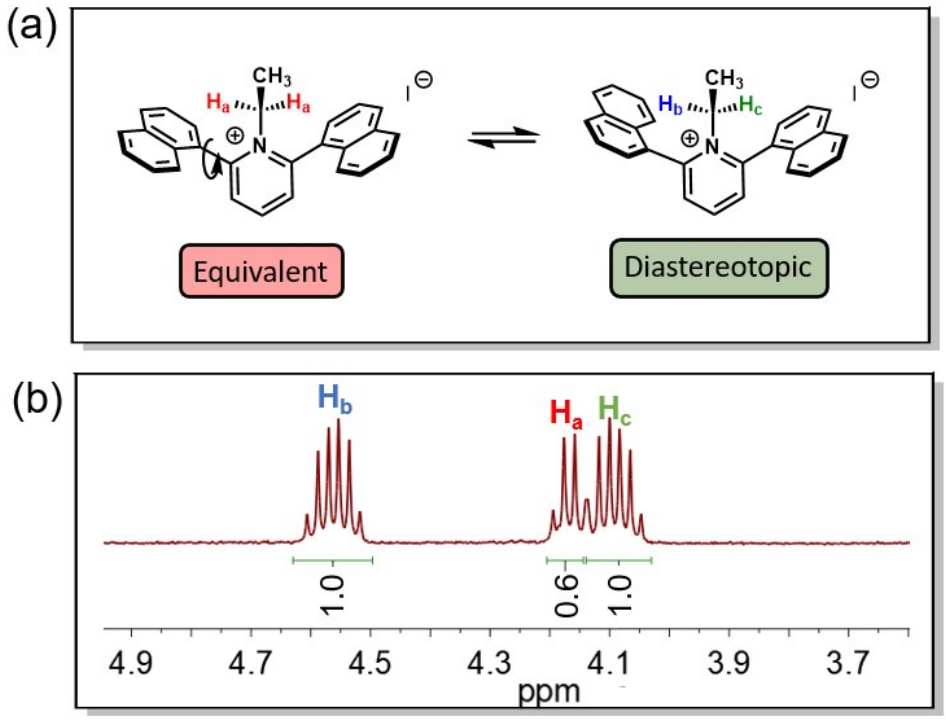

Figure S9. (a) Two atropisomers of **DNP-Et** and their conformations that lead to equivalent and diastereotopic peaks of the methylene protons in ^{1}H NMR. (b) Close up of the three methylene peaks present in the ^{1}H NMR spectrum of **DNP-Et** in CD_2Cl_2 (400 MHz at 25 °C) from δ 4.05-4.70, integrations relative to H_b and H_c, doublet of quartets.

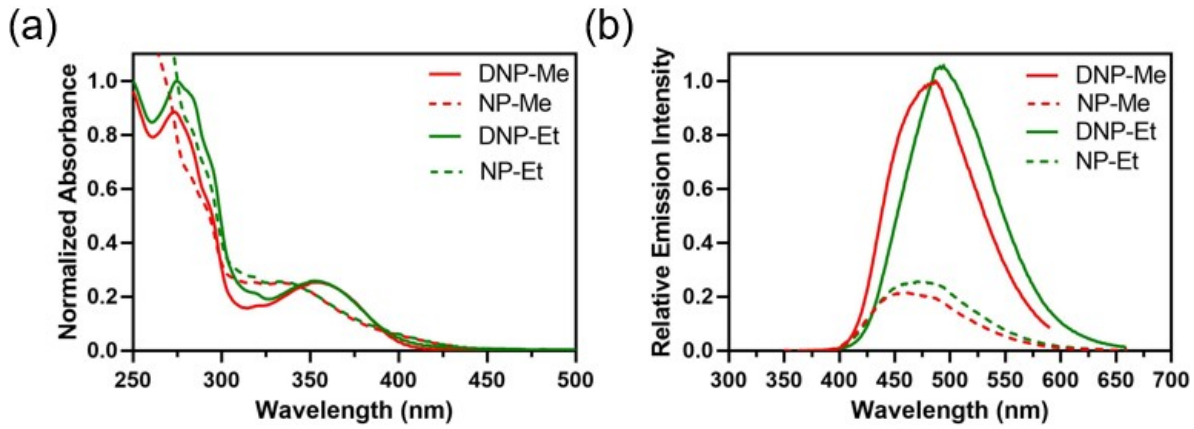

Figure S10. Relative (a) absorbance and (b) emission of **DNP-Me** and **DNP-Et** (solid line) and **NP** (dashed line) compounds in CH_2Cl_2 at 1×10^{-5} M collected at an absorbance of 0.1, excited at λ_{max}.

NMR Spectroscopy

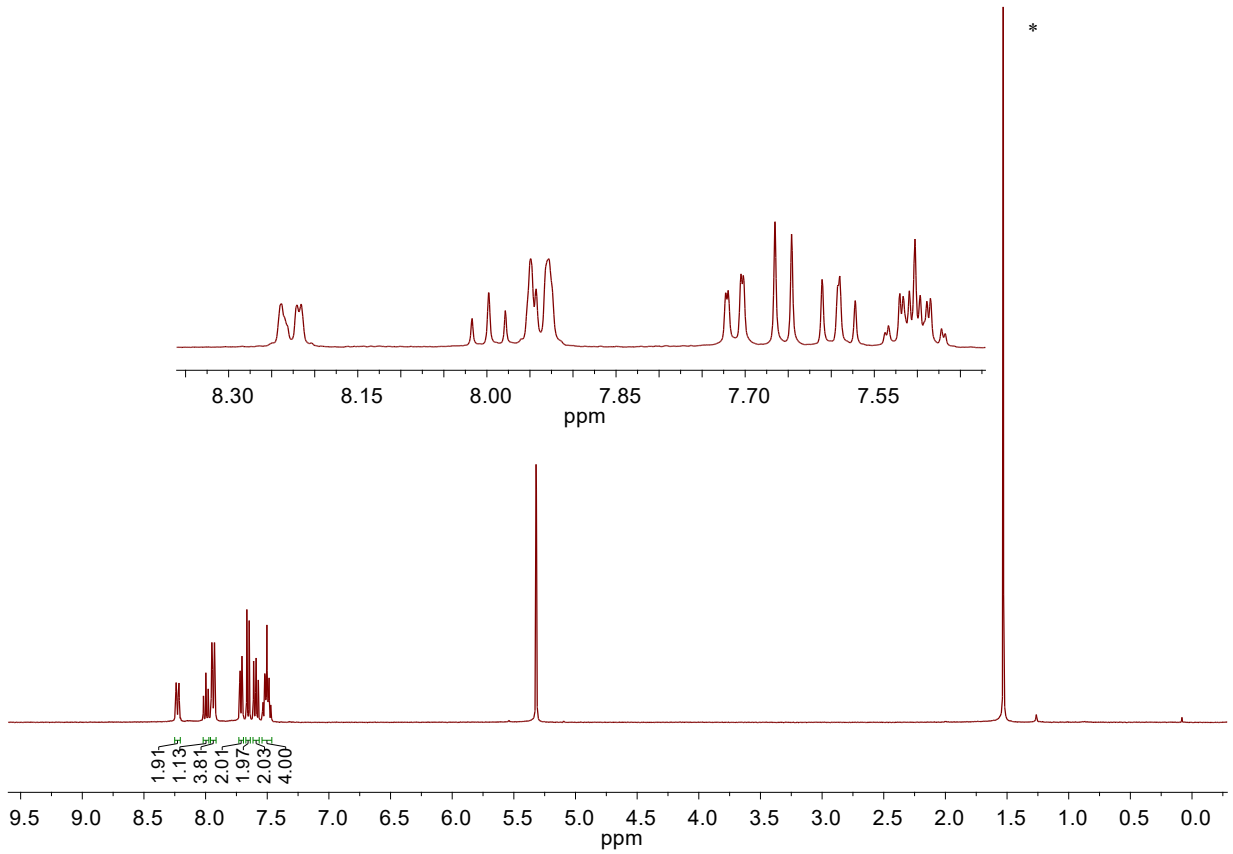

Figure S11. ^{1}H NMR spectrum of **DNP** (300 MHz, CD_2Cl_2) at 25°C. * = water.

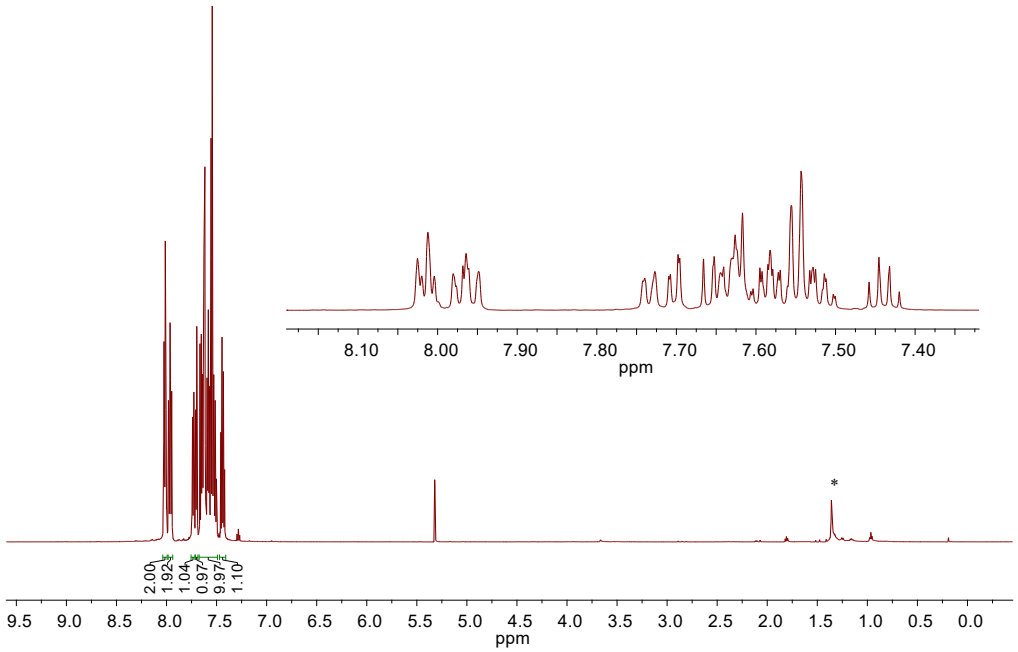

Figure S12. ^{1}H NMR spectrum of **DNP-O** (600 MHz, CD_2Cl_2) at 25°C, * = H grease

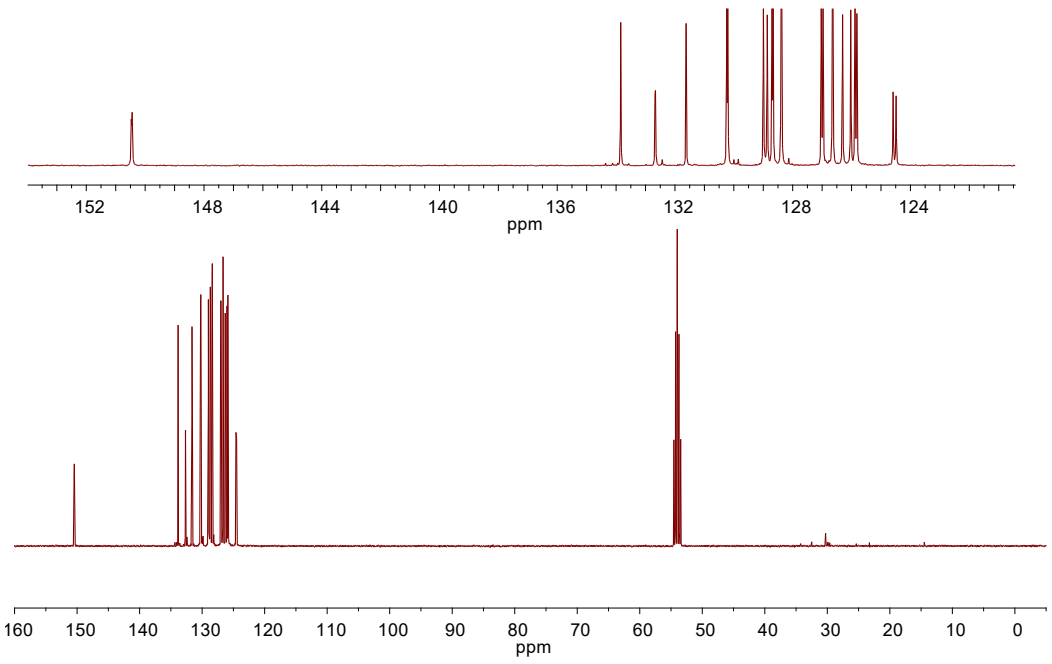

Figure S13.^{13}C NMR spectrum of **DNP-O** (101 MHz, CD_2Cl_2) at 25°C, peak doubling can be observed.

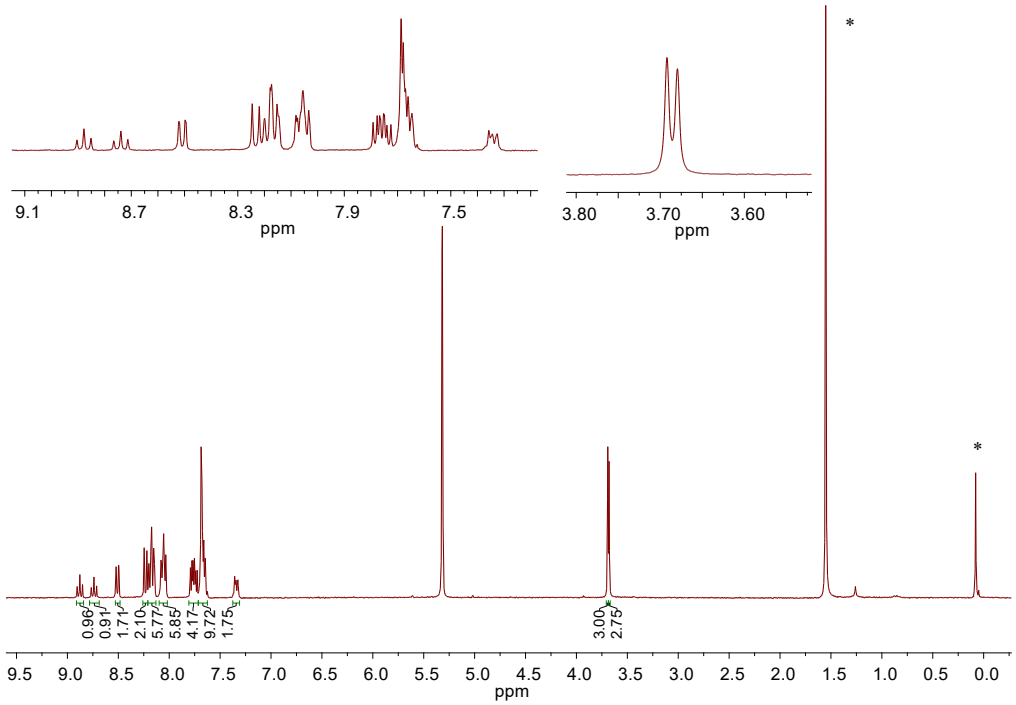

Figure S14. ^{1}H NMR spectrum of **DNP-Me** (300 MHz, CD_2Cl_2) at 25°C, doubling of the peaks can be seen.

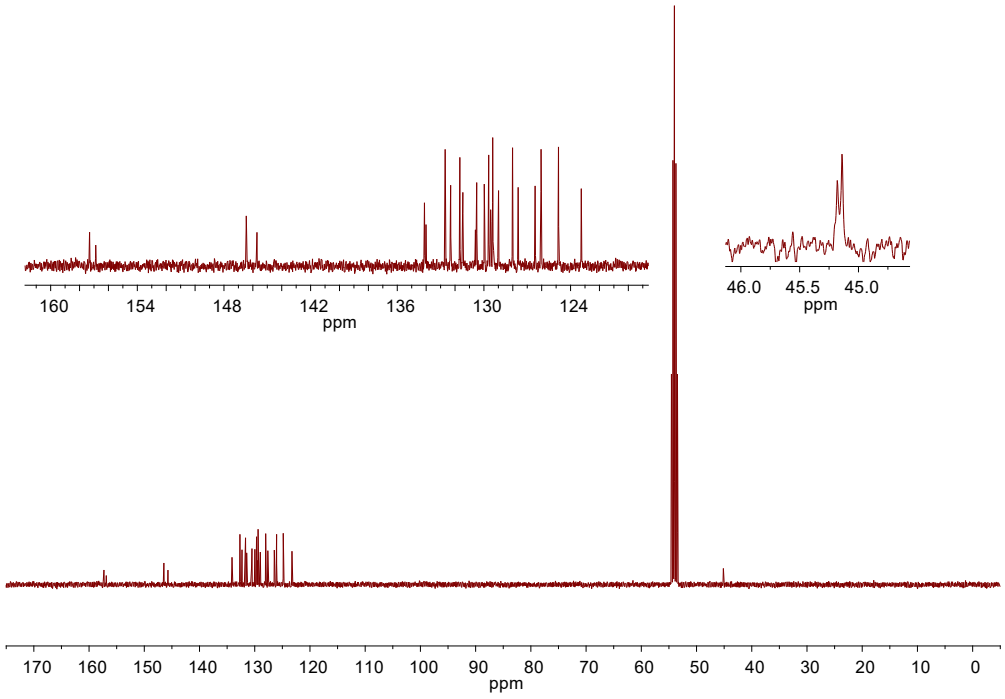

Figure S15. ^{13}C NMR spectrum of **DNP-Me** (101 MHz, CD_2Cl_2) at 25°C, doubling of the peaks can be seen.

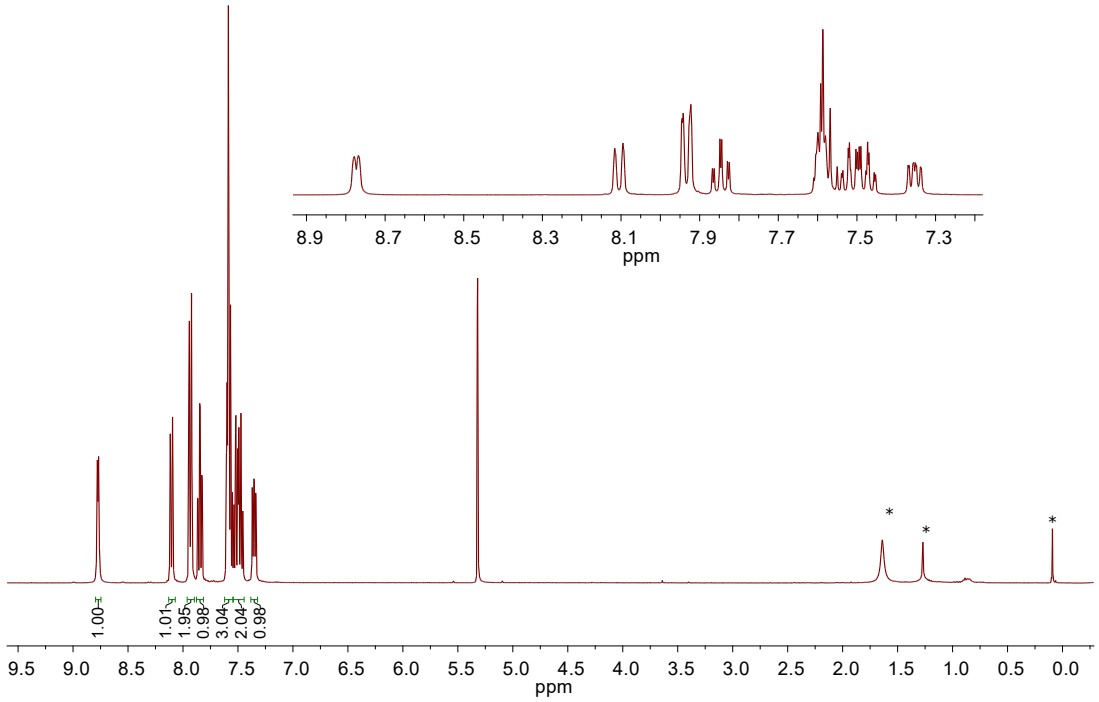

Figure S16. ^{1}H NMR spectrum of **NP** (300 MHz, CD_2Cl_2) at 25°C. * = water, hexanes, H grease.

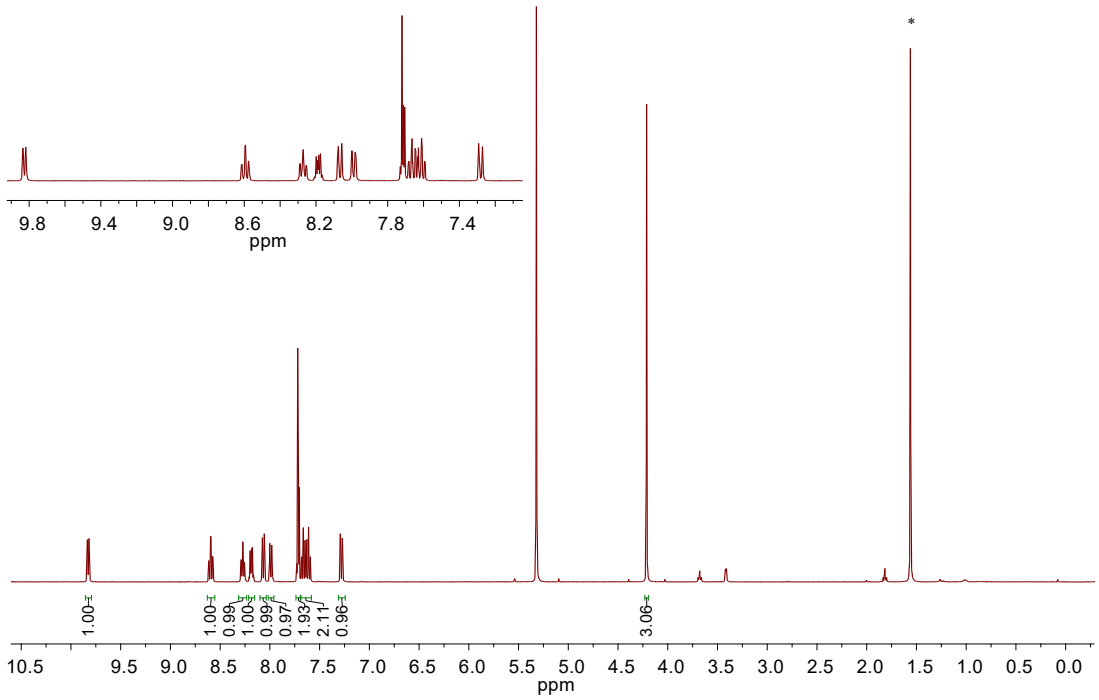

Figure S17. ^{1}H NMR spectrum of **NP-Me** (400 MHz, CD_2Cl_2) at 25°C. * = water.

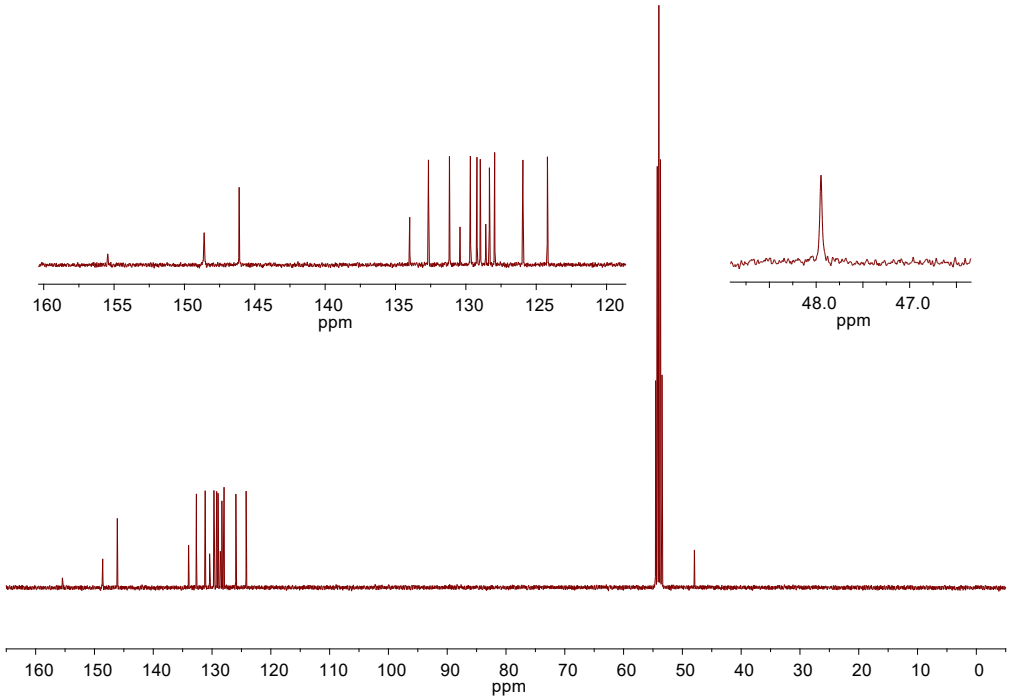

Figure S18. ^{13}C NMR spectrum of **NP-Me** (101 MHz, CD_2Cl_2) at 25°C.

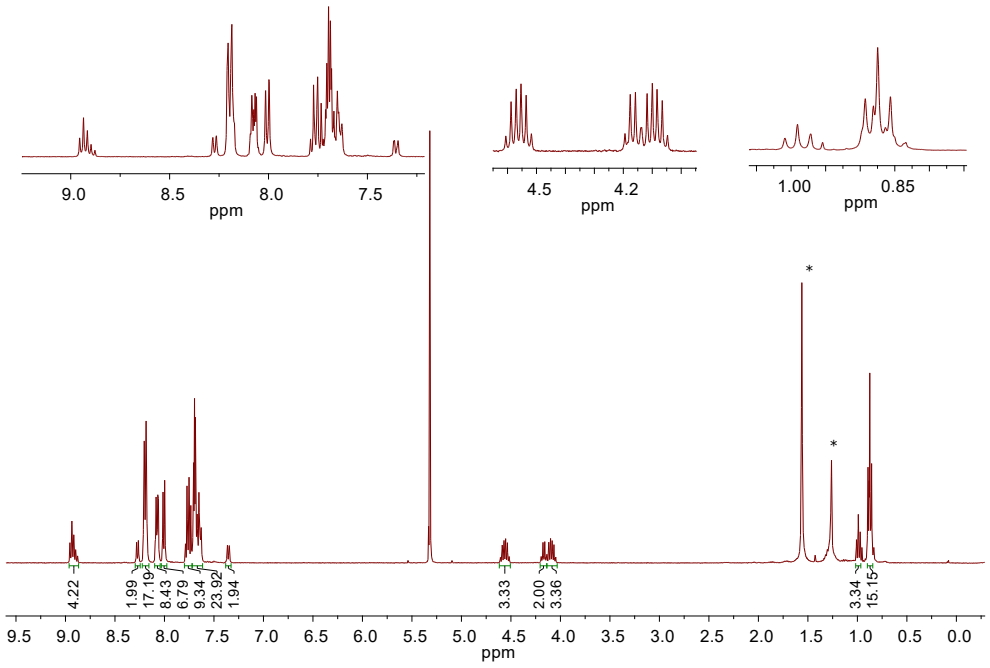

Figure S19. ^{1}H NMR spectrum of **DNP-Et** (400 MHz, CD_2Cl_2) at 25°C, doubling of the peaks can be seen, atropisomers are not in a 1:1 ratio, therefore integration does not accurately represent number of protons.

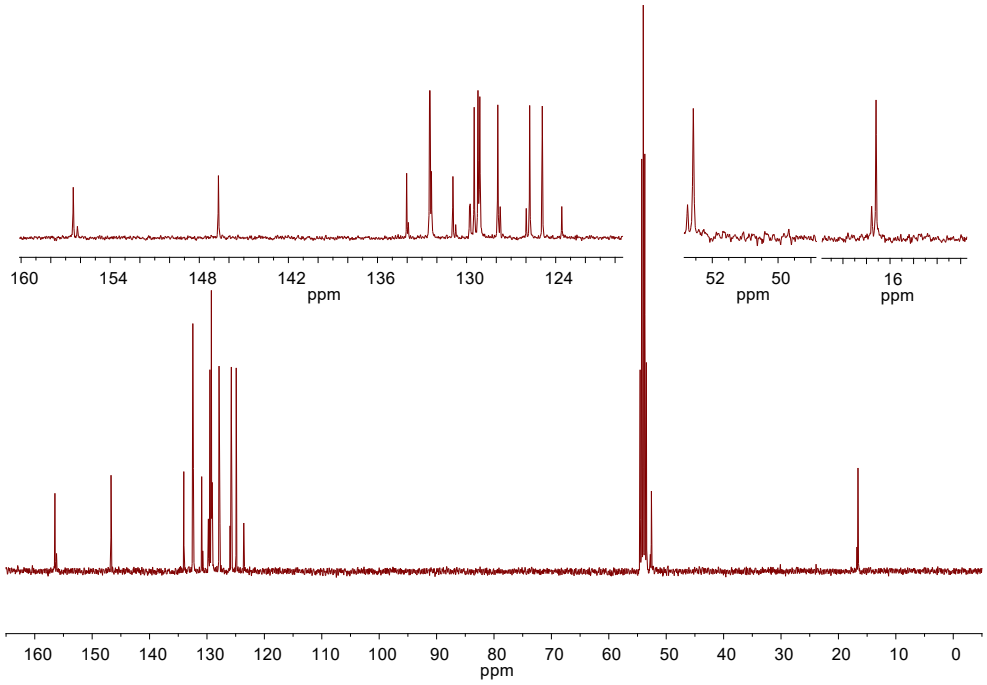

Figure S20. ^{13}C NMR spectrum of **DNP-Et** (101 MHz, CD_2Cl_2) at 25°C, doubling of the peaks can be seen.

* = water, H grease.

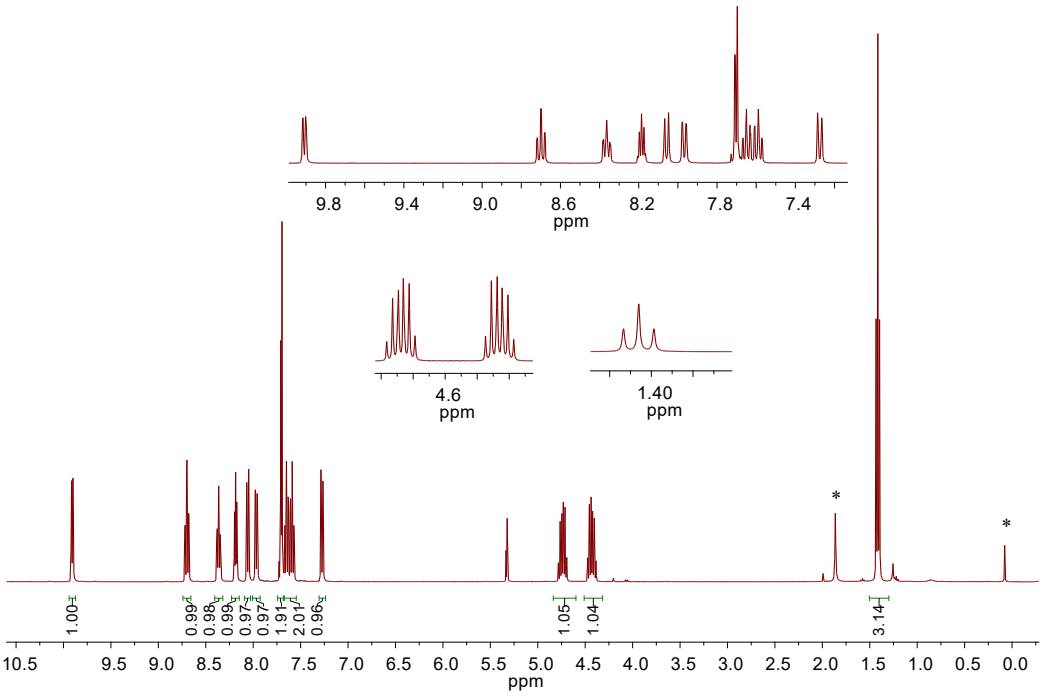

Figure S21. ^{1}H NMR spectrum of **NP-Et** (400 MHz, CD_2Cl_2) at 25°C.

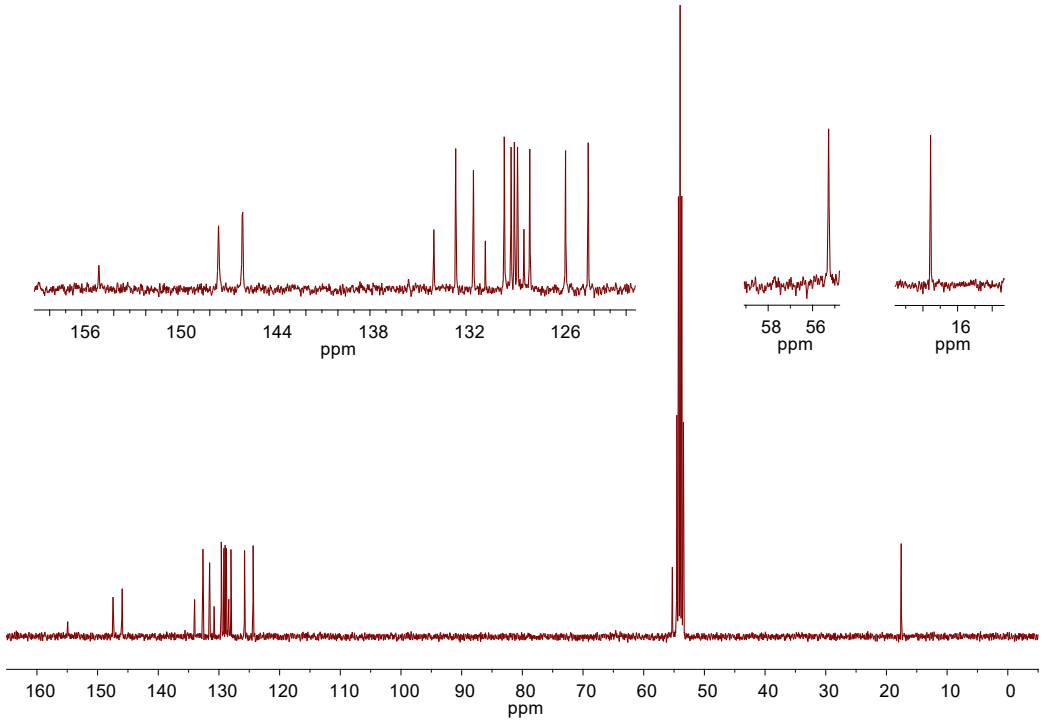

Figure S22. ^{13}C NMR spectrum of **NP-Et** (101 MHz, CD_2Cl_2) at 25°C.

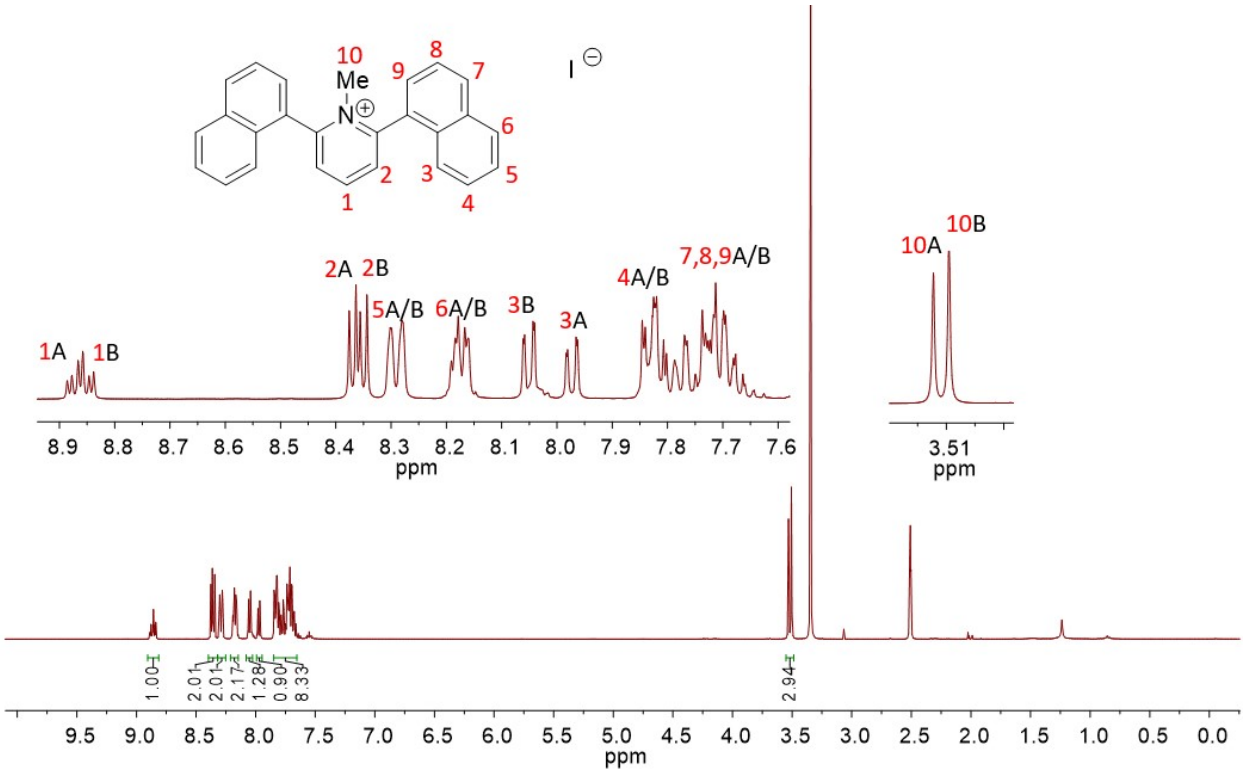

Figure S23. ^{1}H NMR spectrum of DNP-Me (400 MHz, DMSO-d_6) at 25°C. Atropisomer A/B is assigned.

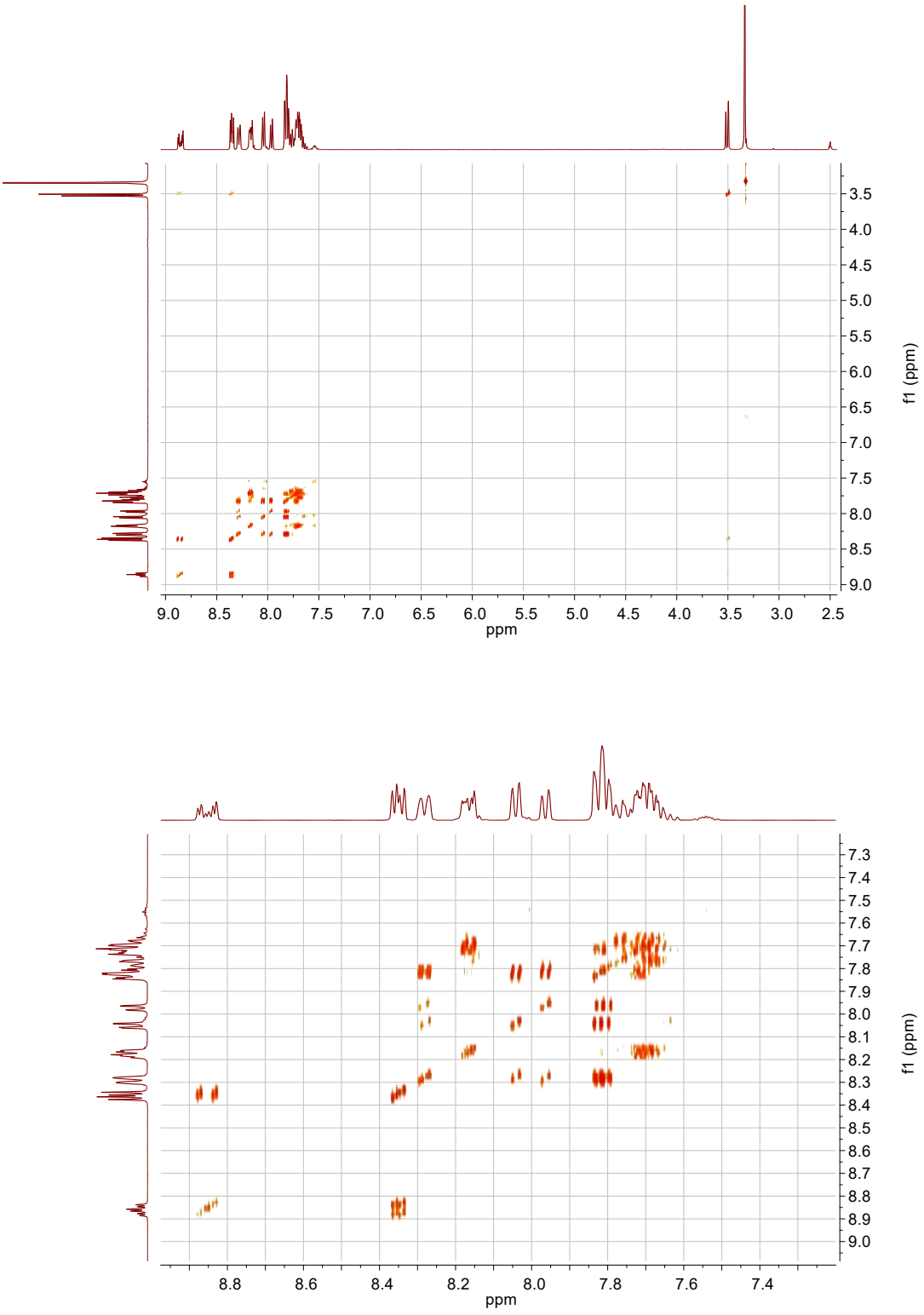

Figure S24. COSY spectrum of **DNP-Me** in DMSO-d_6 at 25°C.

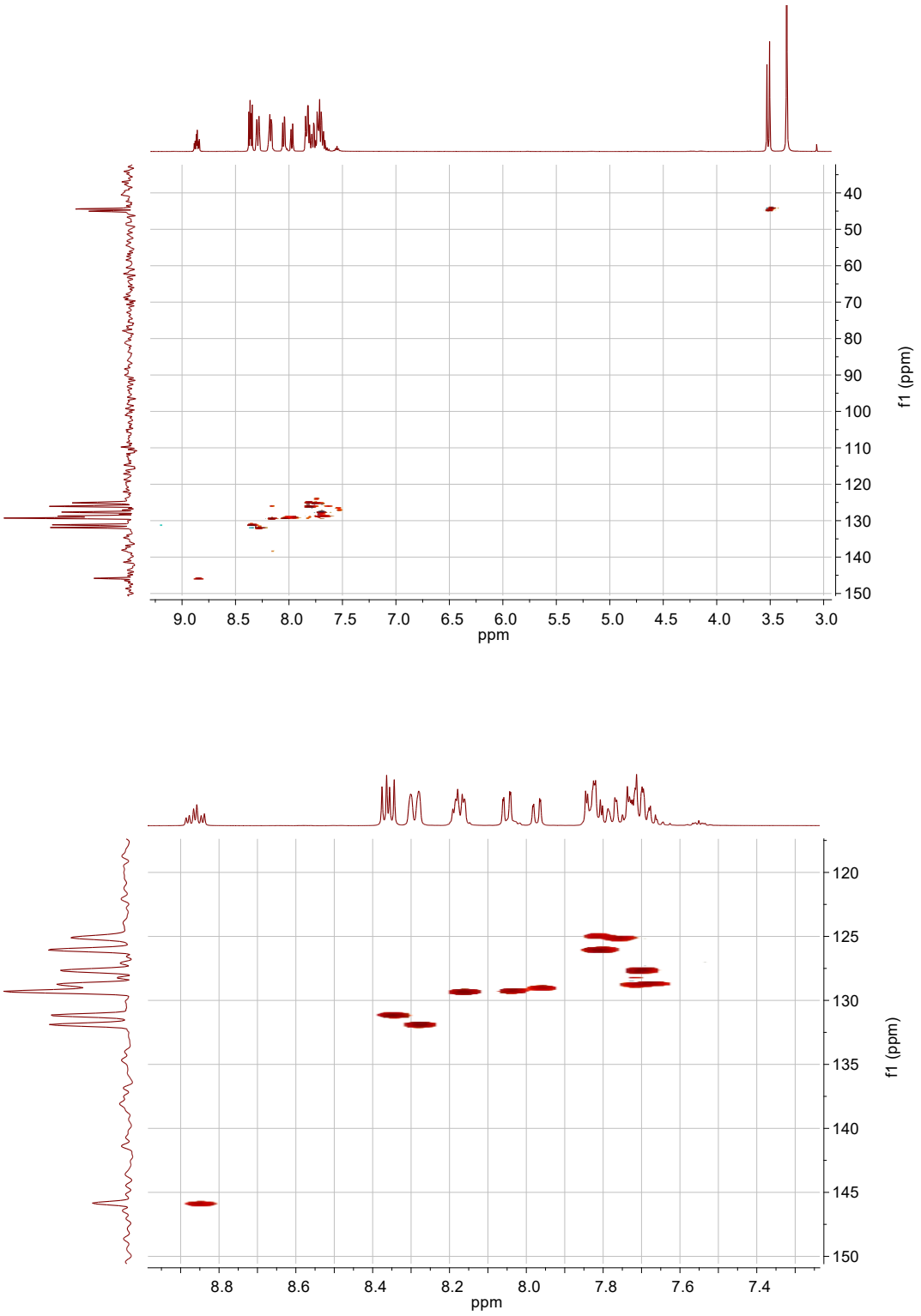

Figure S25. HSQC spectrum of **DNP-Me** in DMSO-d_6 at 25°C.

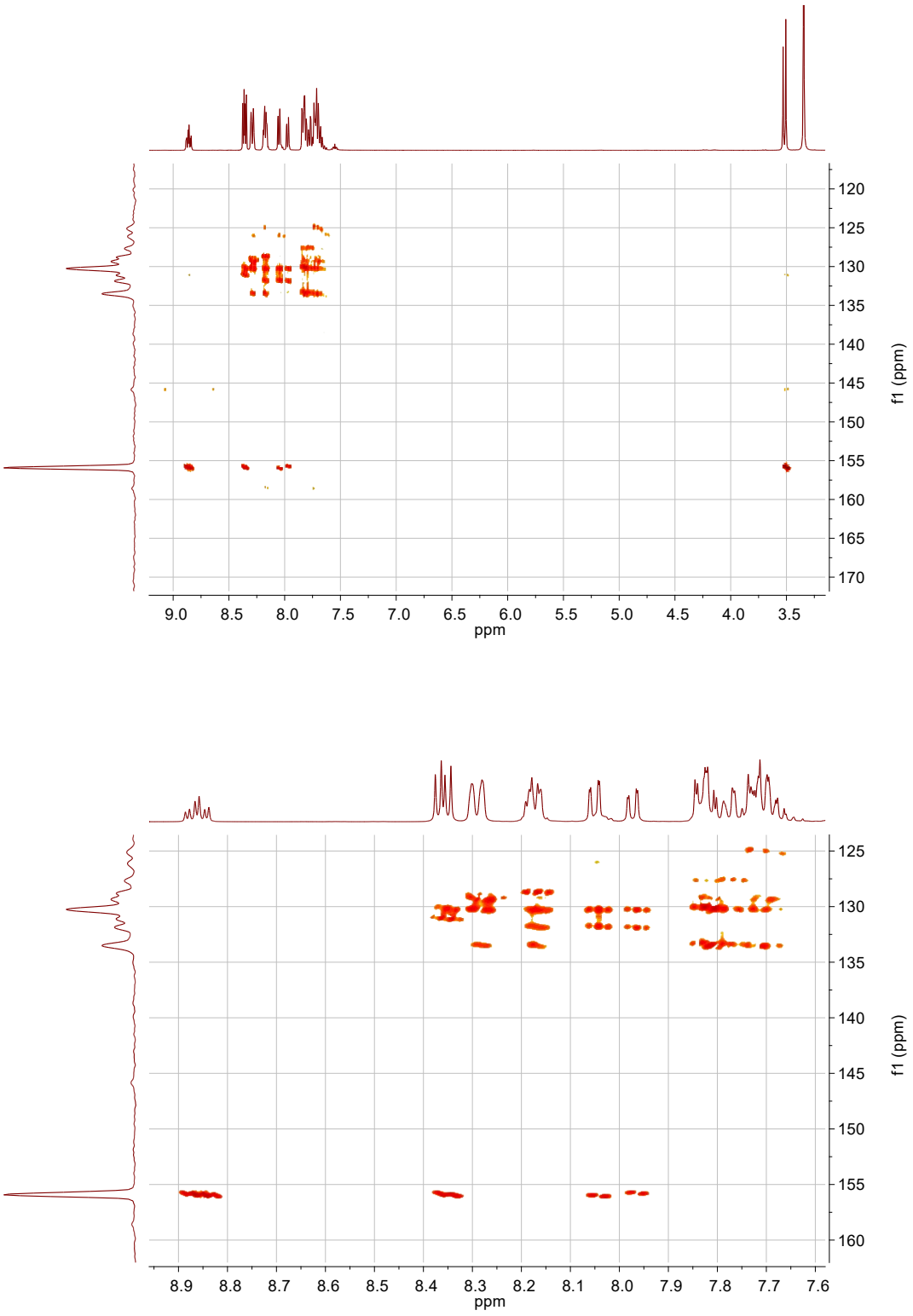

Figure S26. HMBC spectrum of **DNP-Me** in DMSO-d_6 at 25°C.

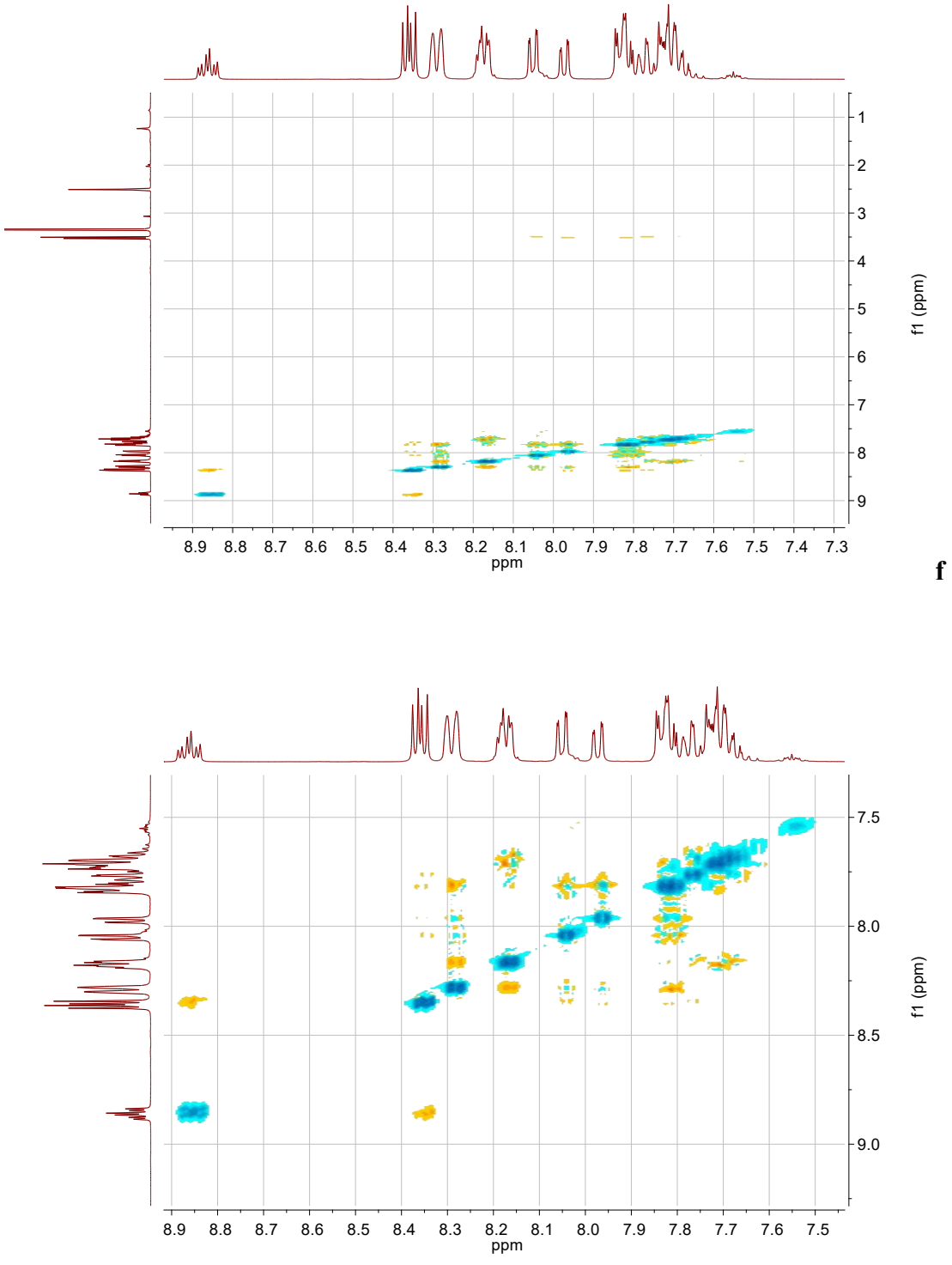

Figure S27. NOESY spectrum of **DNP-Me** in DMSO-d_6 at 25°C.

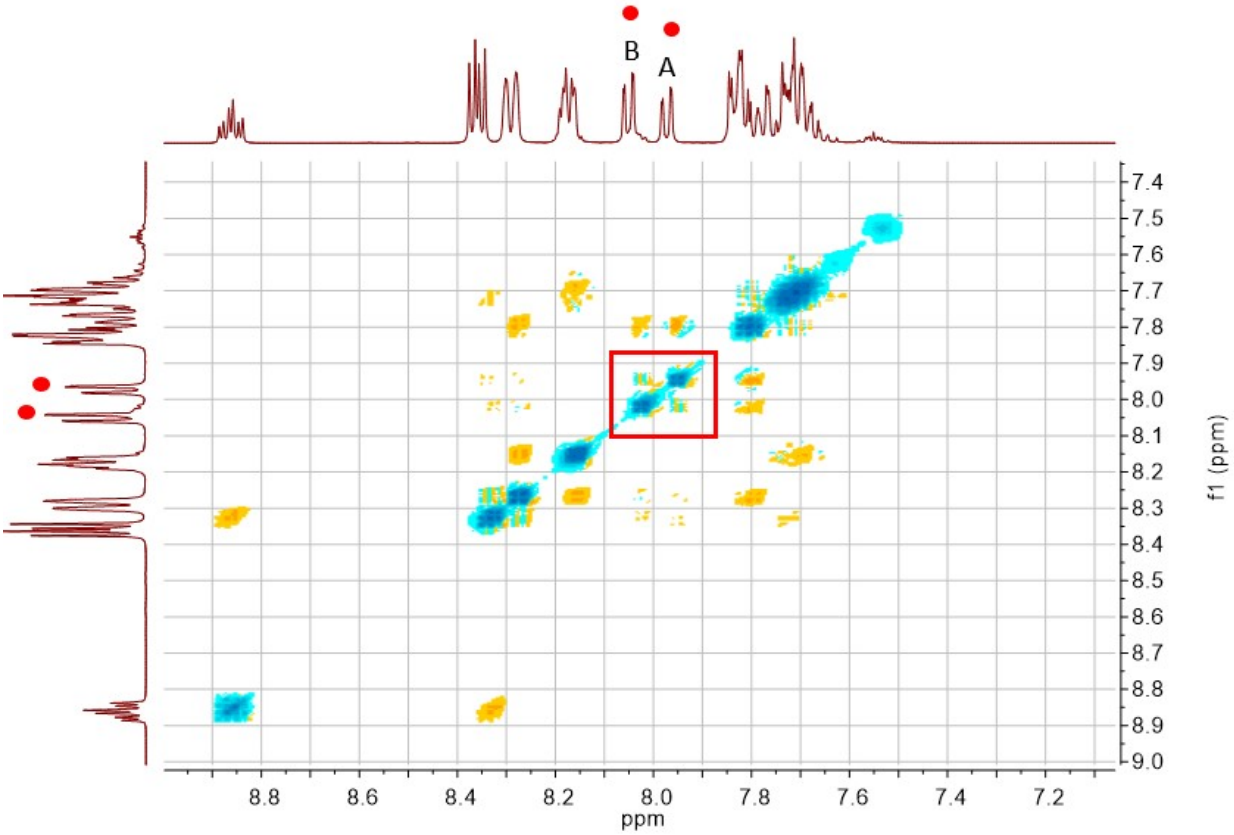

Figure S28. 2D NOESY spectra of **DNP-Me** in DMSO-d_6 at 75°C. Atropisomers A and B are distinguishable at δ = 8.05,7.97. A cross peak is present at elevated temperatures indicating chemical exchange is occurring between A and B.

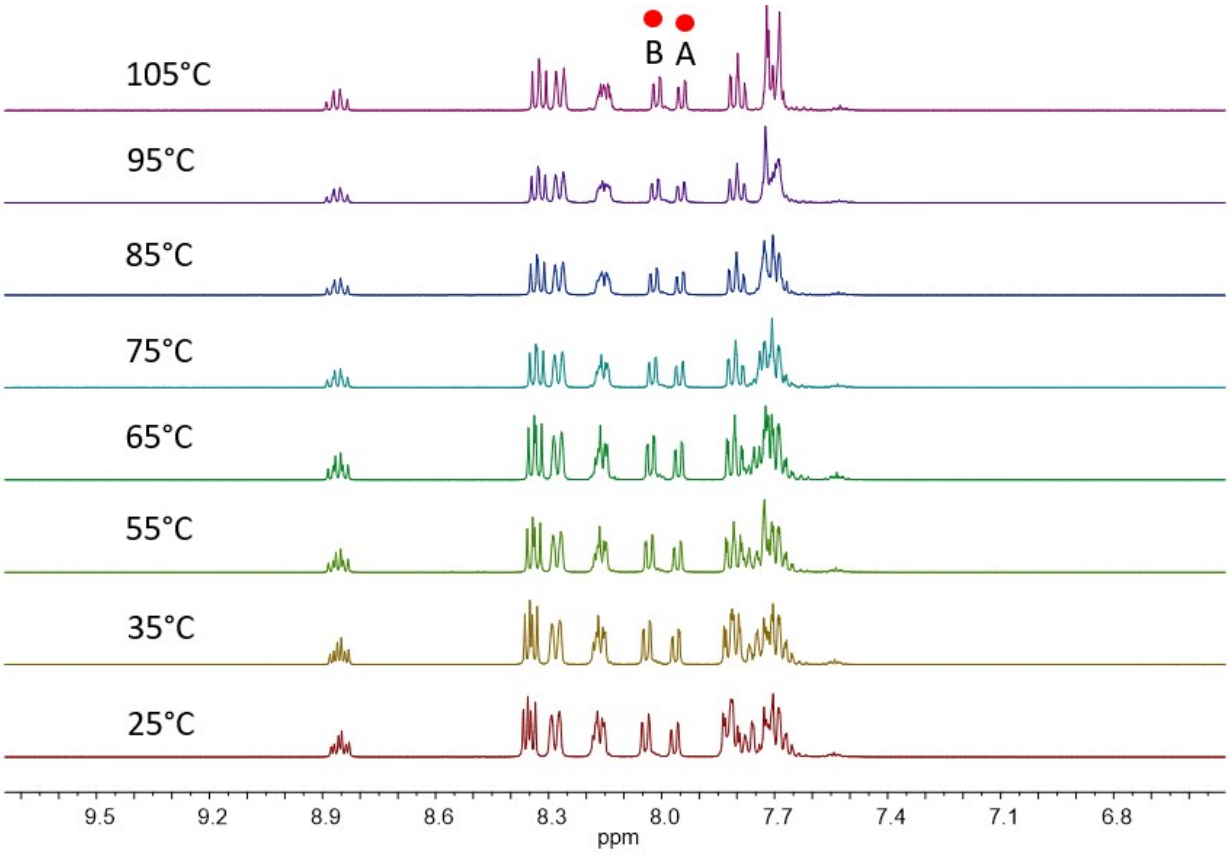

Figure S29. VT NMR of **DNP-Me** (400 MHz, DMSO-d_6) from 25-105 °C. The two red dots correspond to the two distinguishable protons of both DNP-Me atropisomers, no coalescence is seen and peaks stay separate and distinct from 25-105 °C.

Crystallography Data

Table S1. Crystal data and structure refinement for DNP-Me

Empirical formula	$C_{27}H_{22}Cl_2IN$
Formula weight	558.25
Temperature/K	296.15
Crystal system	Triclinic
Space group	P-1
a/Å	7.4594(5)
b/Å	11.1518(7)
c/Å	14.7331(9)
α/°	94.669(4)
β/°	101.035(4)
γ/°	99.434(4)
Volume/Å^3	1178.58(13)
Z	2
ρ_{calc}g/cm^3	1.573
μ/mm^{-1}	1.600
F(000)	556.0
Crystal size/mm^3	0.4 × 0.38 × 0.228
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	2.836 to 61.154
Index ranges	$-10 \leq h \leq 10$, $-15 \leq k \leq 15$, $-21 \leq l \leq 21$
Reflections collected	25789
Independent reflections	7074 [R_{int} = 0.0349, R_{sigma} = 0.0351]
Data/restraints/parameters	7074/0/281
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R_1 = 0.0381, wR_2 = 0.0973
Final R indexes [all data]	R_1 = 0.0439, wR_2 = 0.1009
Largest diff. peak/hole / e Å^{-3}	1.72/-1.71