# Supporting Information

Large negative magneto-LC effects induced by racemic dimerization of liquid crystalline nitroxide radicals with terminal cyano group

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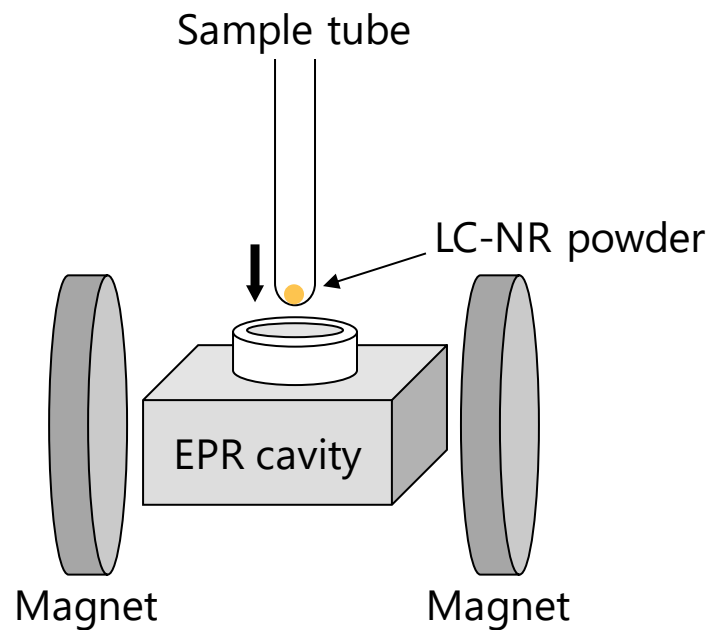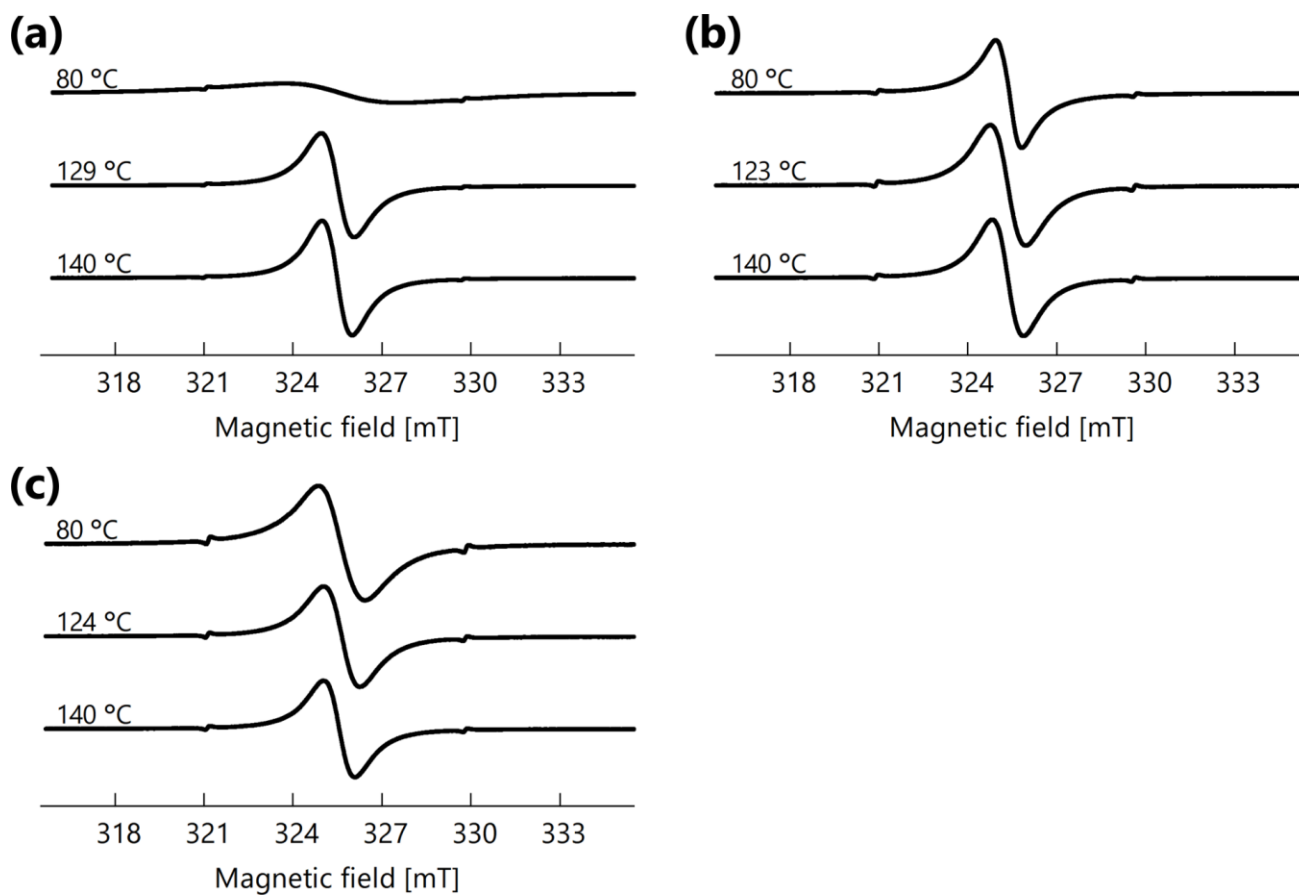
**Fig. S1** Experimental setup to measure EPR spectra.



**Fig. S2** Selected EPR spectra of (a) (±)-**3**, (b) (2*R*,5*R*)-**3** and (c) (±)-**4** measured at various temperatures from the crystalline phase (top) to the isotropic phase (bottom) through the liquid crystalline phase.
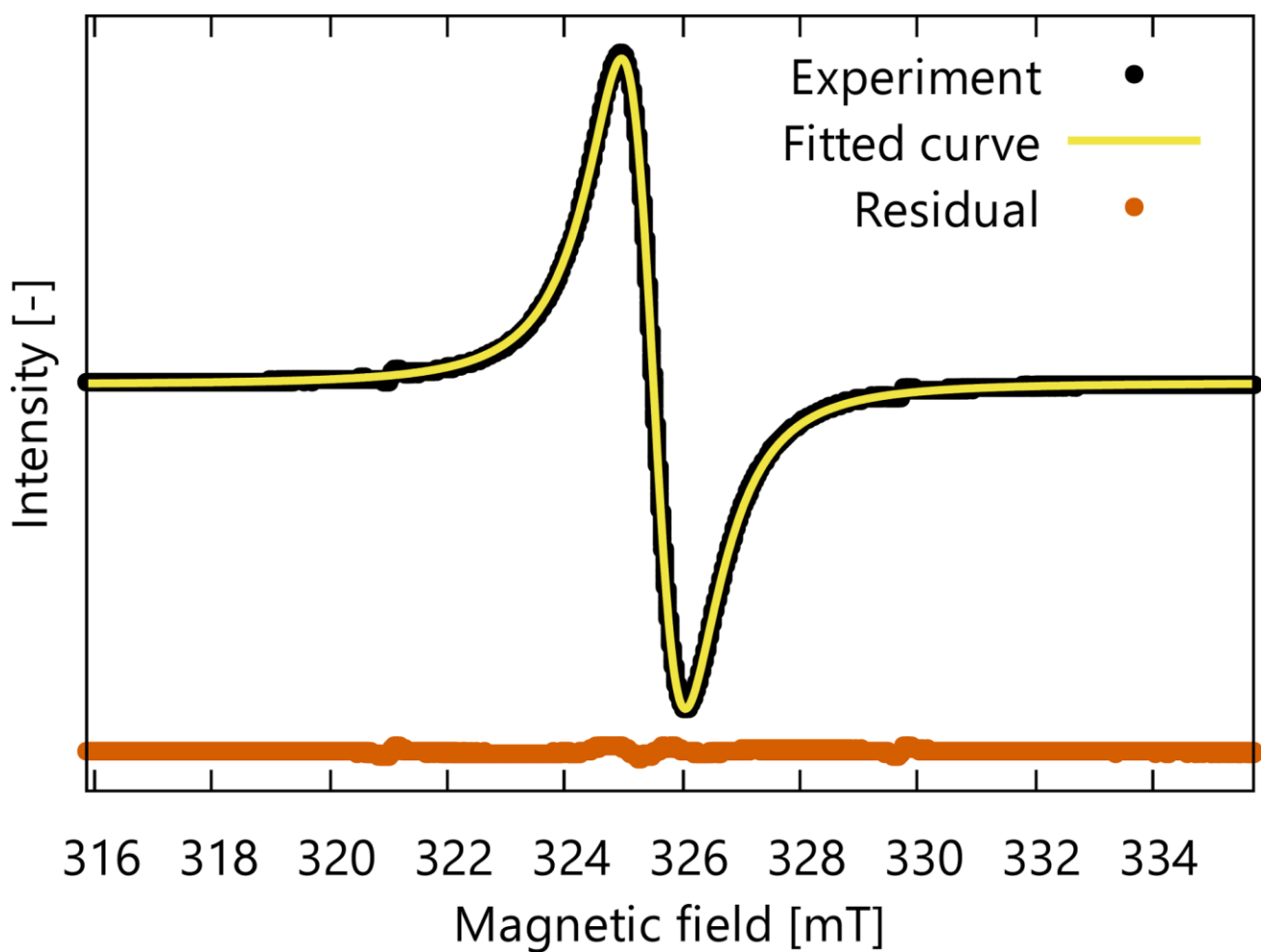
**Fig. S3** Selected EPR spectrum of (±)-**3** at 129 °C in heating process. Experimental data (black circles), a fitted curve of differential Lorentzian function (yellow solid line) and little residuals between them (red circles) are shown.
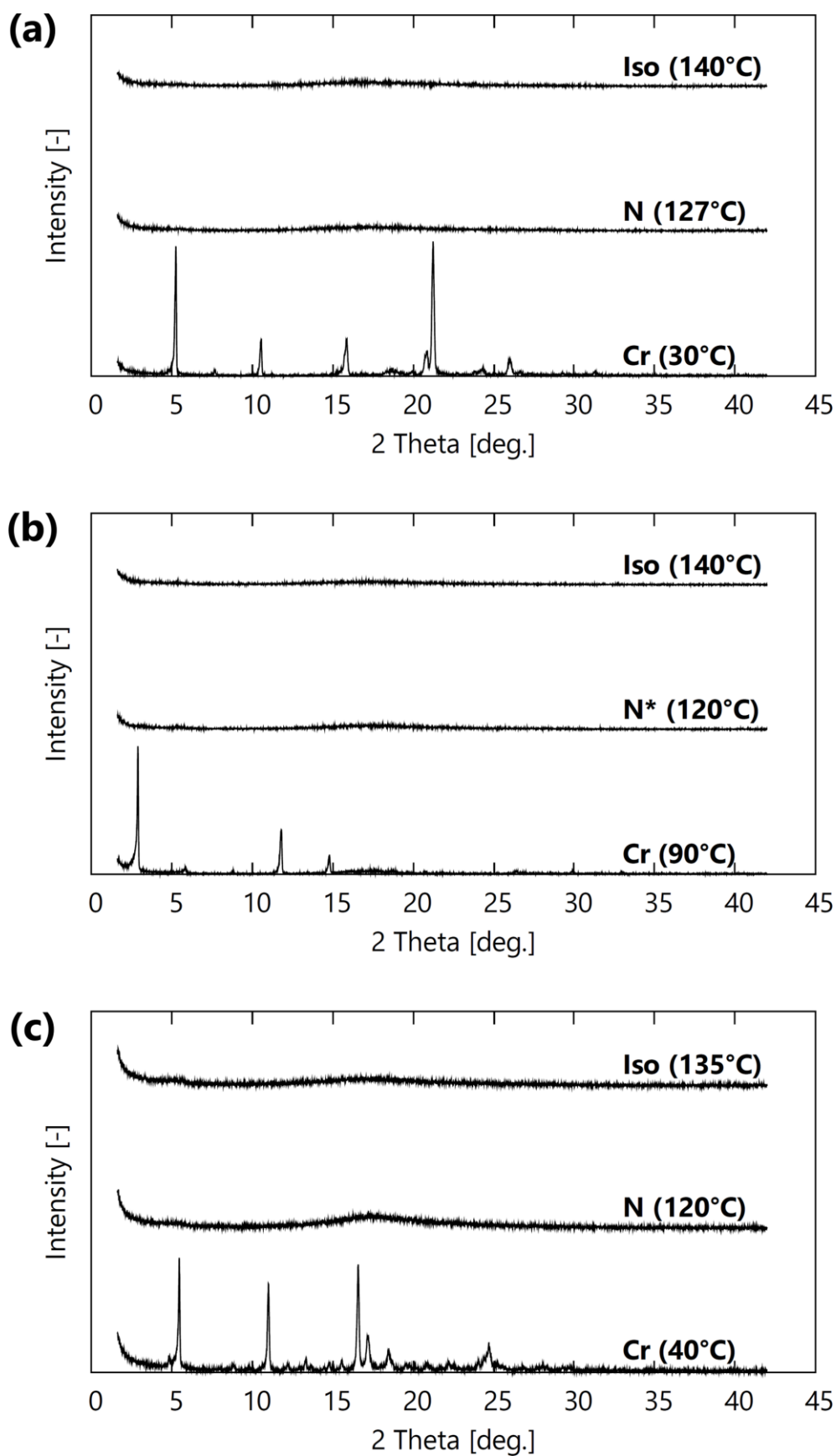
**Fig. S4** XRD patterns of (a) (±)-**3**, (b) (2*R*,5*R*)-**3** and (c) (±)-**4** in Cr, LC and Iso phases in the heating processes.
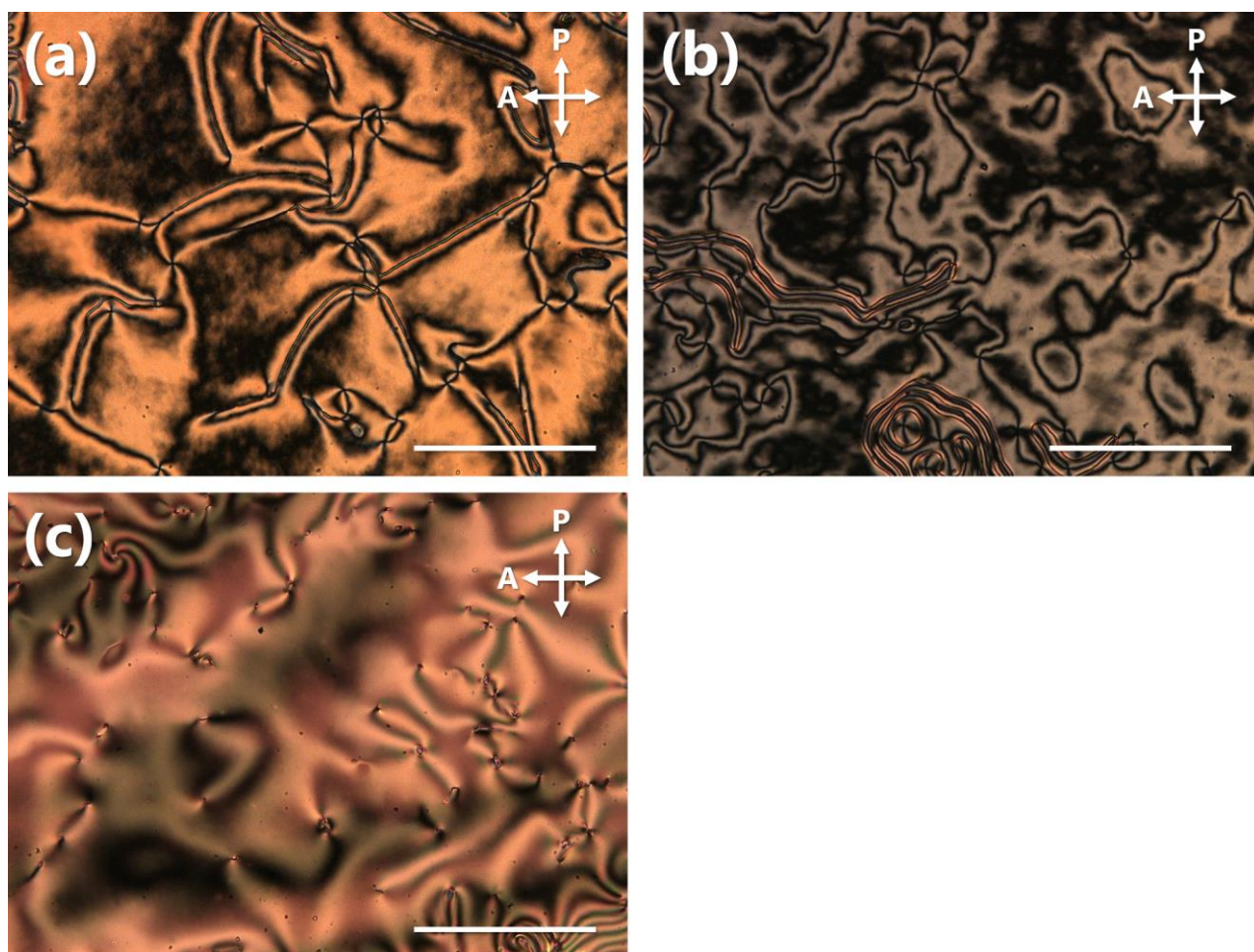
**Fig. S5** Polarized optical micrographs of Schlieren textures for the N phase of (±)-**2** at 90 °C in cells coated with (a) JALS-204, (b) hexadecyltrimethylammonium bromide ($C_{16}$TAB) and (c) CYTOP. The orientations of polarizer (P) and analyzer (A) are shown. Scale bars correspond to 200 μm.
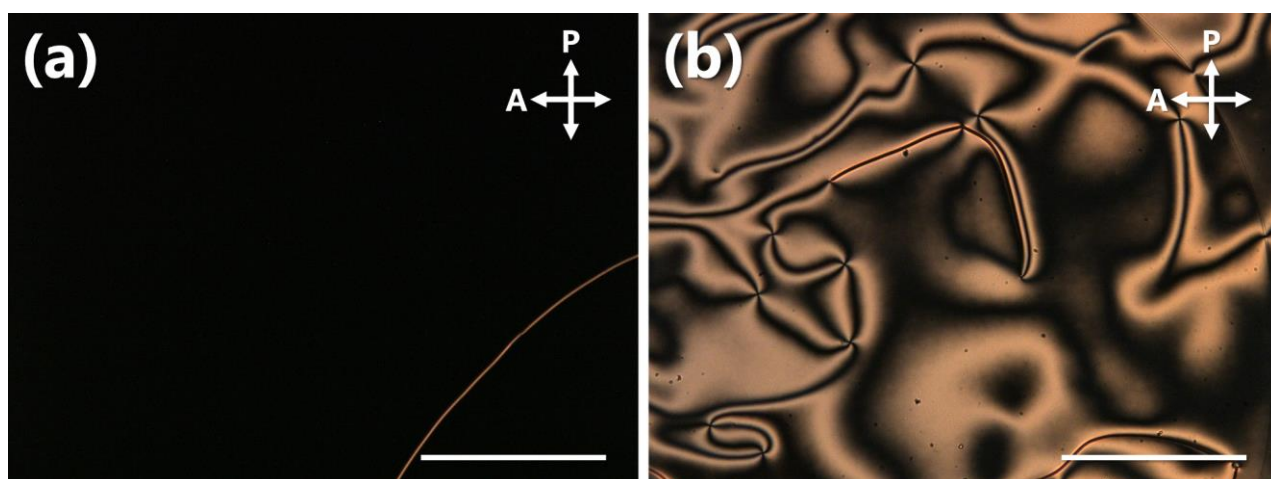


**Fig. S6** Polarized optical micrographs of (±)-**3**. (a) A pseudo isotropic state for the N phase at 125 °C in a cell coated with $C_{16}$TAB. The bottom-right corner in the image contains no sample. (b) A Schlieren texture for the N phase at 125 °C in a cell coated with CYTOP. The orientations of polarizer (P) and analyzer (A) are shown. Scale bars correspond to 200 μm.

*Determination of the crystal structure of (±)-3*

Crystals of (±)-**3** suitable for XRD studies were prepared by the recrystallization from hexane and Et$_2$O, and analyzed using an X-ray diffractometer. The X-ray crystal structure of (±)-**3** was solved by direct methods and refined using the full-matrix least-squares method. In subsequent refinements, the function $\sum \omega (F_o^2 - F_c^2)^2$ was minimized, where $F_o$ and $F_c$ are the observed and calculated structure factor amplitudes, respectively. The positions of non-hydrogen atoms were determined from difference Fourier electron-density maps and refined anisotropically. All calculations were performed with the Crystal Structure crystallographic software package.
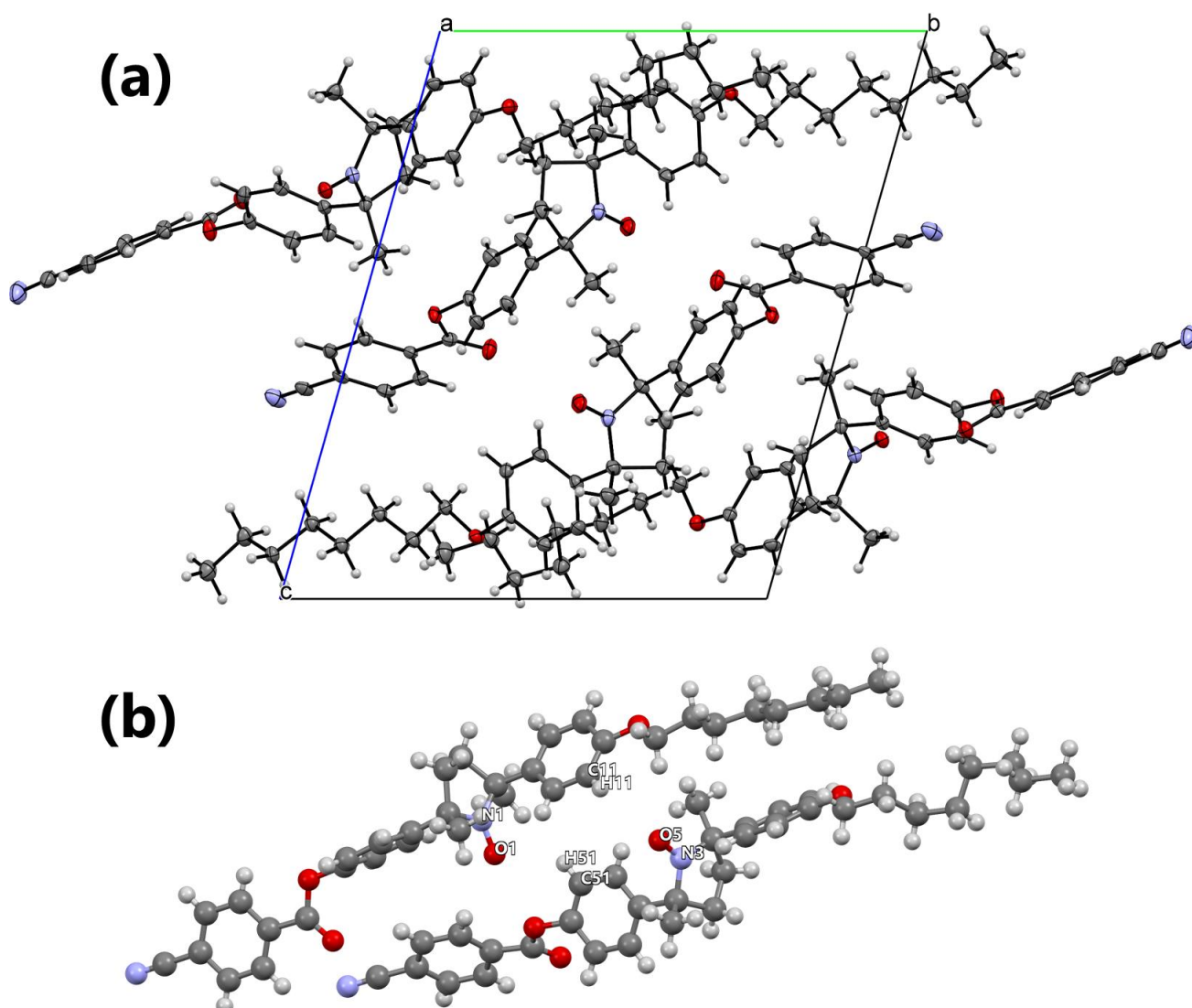


**Fig. S7** (a) Crystal structure of (±)-**3** determined by X-ray crystallographic analysis and (b) relative position of a pair of molecules in the crystal showing intermolecular interactions between the NO radical group and the methyl group.

**Table S1** Calculated spin density values of (±)-**3**.

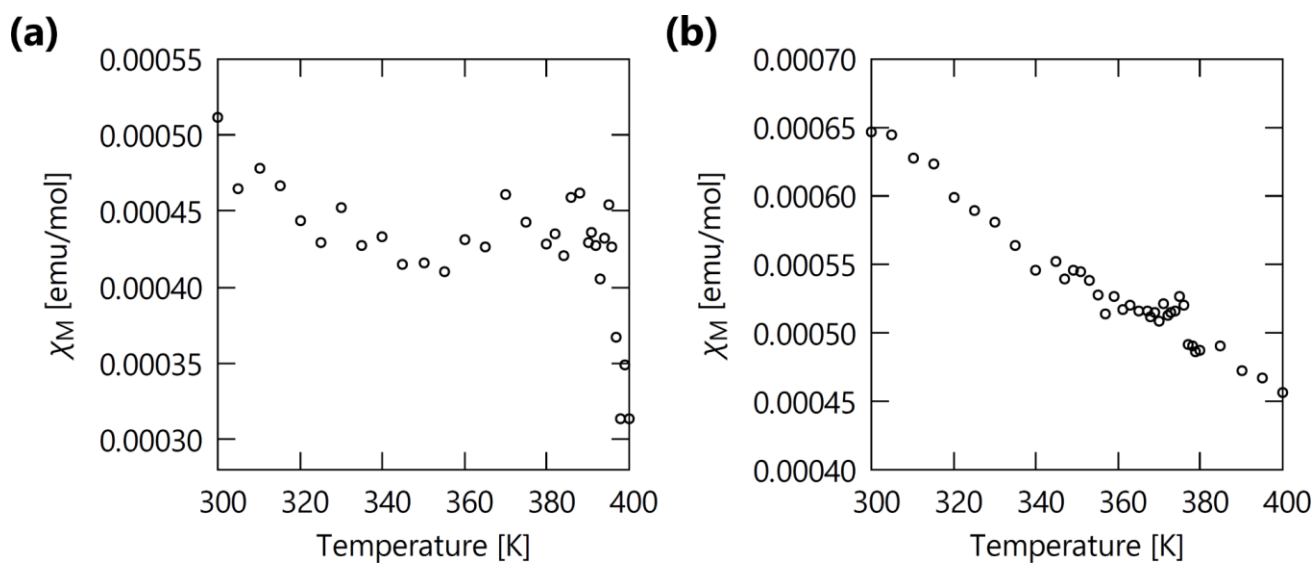| Atom | Spin density |
|------|--------------|
| N1 | 0.456679 |
| O1 | 0.479352 |
| C11 | 0.003377 |
| H11 | 0.000931 |
| N3 | −0.447483 |
| O5 | −0.491305 |
| C51 | −0.001340 |
| H51 | 0.000597 |



**Fig. S8** Temperature dependences of molar magnetic susceptibility ($\chi_M$) observed by SQUID of (a) (±)-**3** and (b) (2$R$,5$R$)-**3** at a field of 0.05 T in the first heating process.
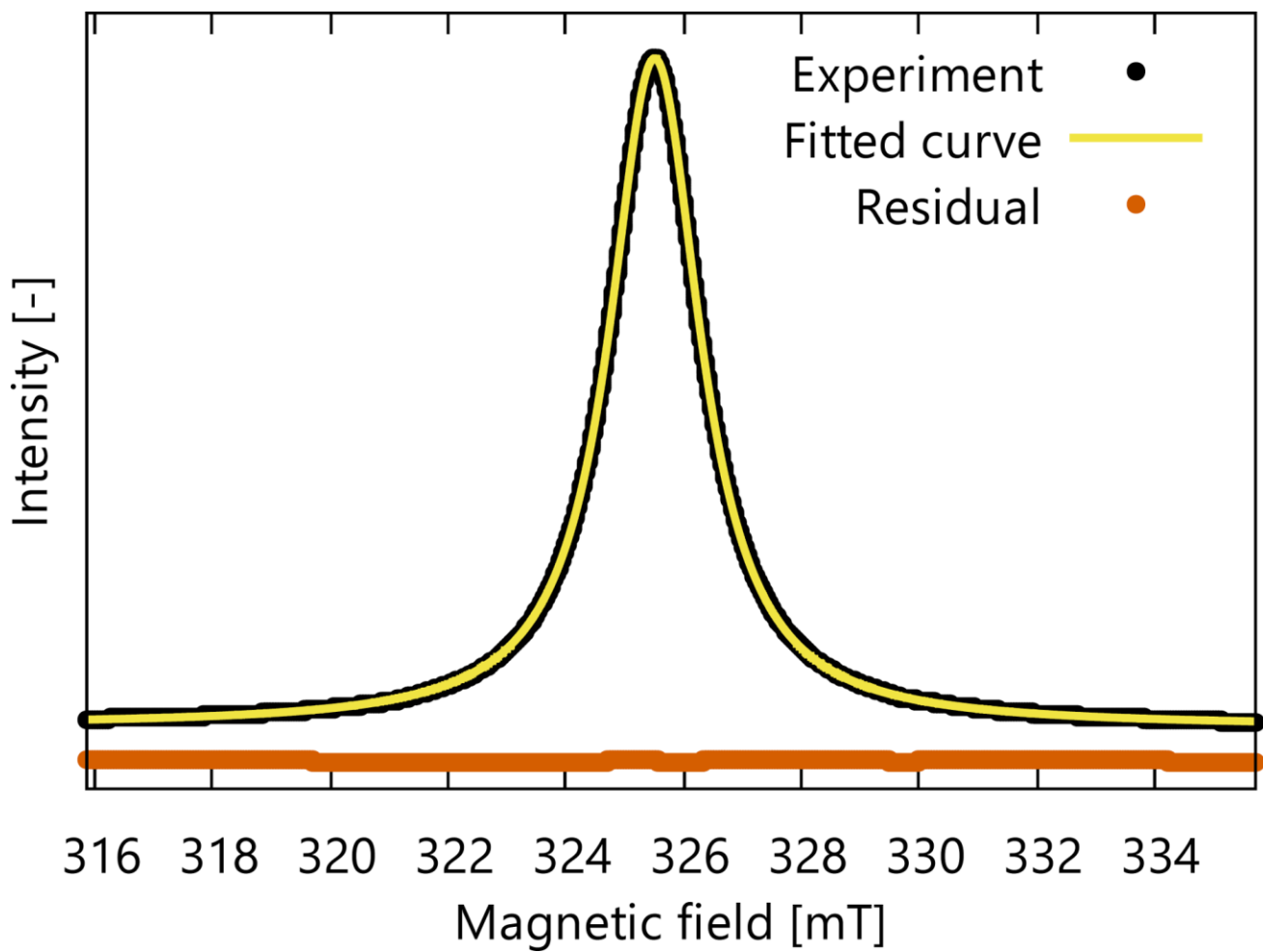
**Fig. S9** Selected EPR spectrum in the integral form of (±)-**3** at 129 °C in heating process. Experimental data (black circles), a fitted curve of Voigt function (yellow solid line) and little residuals between them (red circles) are shown.