Figure S1: Field dependence of magnetization at 1.4K (black circles), 2.45K (blue squares) and 4.4K (red stars).

Figure S2: Angular dependence of resonance fields for S=35/2, D=-0.03 cm⁻¹, E=0.0015 cm⁻¹. Three bands can be distinguished, corresponding to the principal transitions, the B₀/2 ones and the B₀/3 ones.
**Figure S3:** Energy levels of the $S = 35/2$ state for $\theta = 54^\circ$ and $\phi = 0^\circ$. The red arrows indicate allowed transitions at W-band for the $S = 35/2$, the grey arrows the forbidden ones.
**Figure S4:** $\Delta B_0$ and $\Delta B$ linewidth (see text) assumed for the observed single transitions of the $S=3\frac{3}{2}$ multiplet as a function of $m$, at $T=25$ K with $\theta = \phi = 0^\circ$.

**Figure S5:** $\Delta B_0$ linewidth assumed for the observed single transitions of the $S=3\frac{3}{2}$ multiplet as a function of $m$, at $T=10$ K with $\theta = \phi = 90^\circ$. 
Figure S6: X-band EMR powder spectra of Fe$_{19}$ (black) recorded at different temperatures with a power of 65.57 µW and simulations (red), sum of the $S = 35/2$ (dashed blue) and $S = 33/2$ (dashed green) contributions.
**Figure S7:** Energy levels of the $S = 35/2$ (blue) and $S = 33/2$ (magenta) for $\theta = 0^\circ$ and $\phi = 90^\circ$. The red arrows indicate allowed transitions at X-band for the $S = 35/2$, the grey arrows the forbidden ones.

**Figure S8:** Energy levels of the $S = 35/2$ (blue) and $S = 33/2$ (magenta) for $\theta = 90^\circ$ and $\phi = 90^\circ$. The red arrows indicate allowed transitions at X-band for the $S = 35/2$, the grey arrows the forbidden ones.
Figure S9: Energy levels of the $S = 35/2$ (blue) and $S = 33/2$ (magenta) for $\theta = 0^\circ$ and $\phi = 90^\circ$. The red arrows indicate allowed transitions at W-band for the $S = 35/2$, the grey arrows the forbidden ones.
Figure S10: Energy levels of the $S = 35/2$ (blue) and $S = 33/2$ (magenta) for $\theta = 90^\circ$ and $\phi = 90^\circ$.

The red arrows indicate allowed transitions at W-band for the $S = 35/2$, the grey arrows the forbidden ones.