Supplementary Information

Ion dynamics in *closo*-hydroborates $Ag_2[B_{10}H_{10}]$ and $Tl_2[B_{10}H_{10}]$: ^1H, ^{11}B and ^{205}Tl NMR studies

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Table S1. Results of the elemental analysis for $Ag_2[B_{10}H_{10}]$

Elements	H	B	Ag
Calc. (wt. %)	3.02	32.38	64.61
Exp. (wt. %)	2.97	32.35	64.59

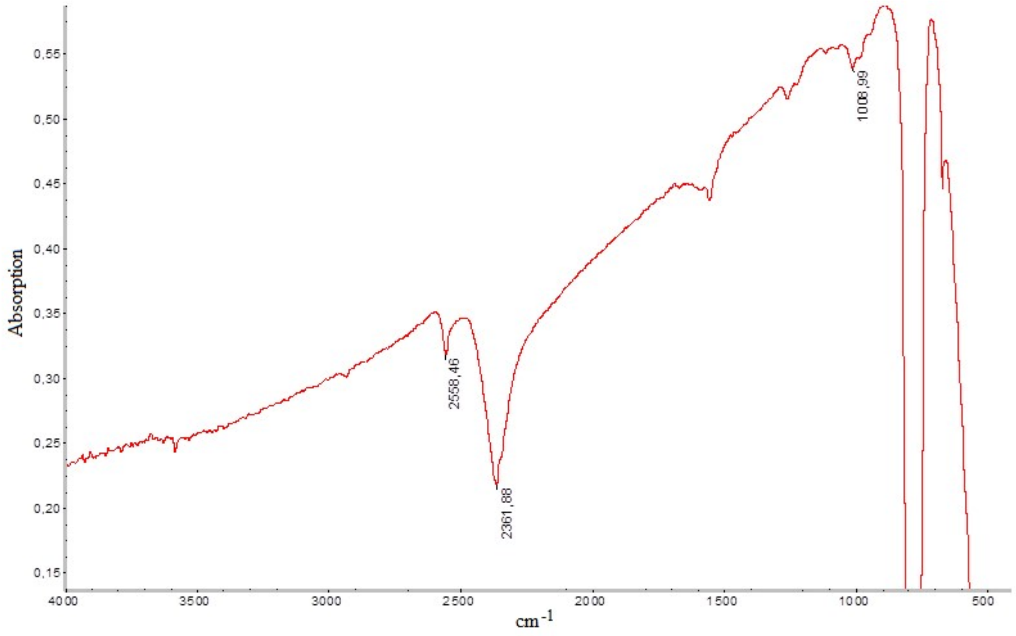

Fig. S1. IR spectrum of $Ag_2[B_{10}H_{10}]$: $\nu(BH)_{MHB}$ = 2558 cm^{-1}, $\nu(BH)$ = 2362 cm^{-1}, $\delta(BBH)$ = 1009 cm^{-1}.

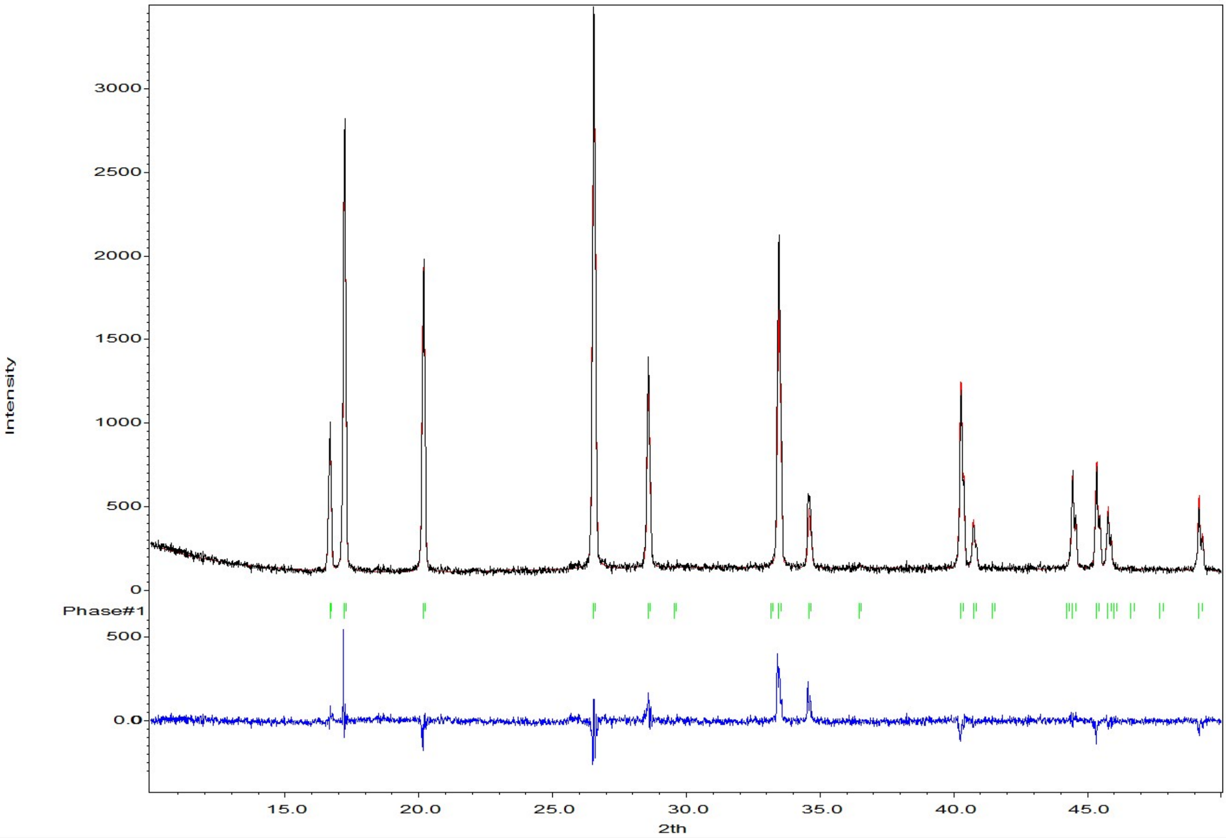

Fig. S2. Room-temperature X-ray powder diffraction pattern for $Ag_2[B_{10}H_{10}]$. Black: experimental; red: calculated; blue: the difference. Vertical bars show the calculated positions of Bragg peaks.

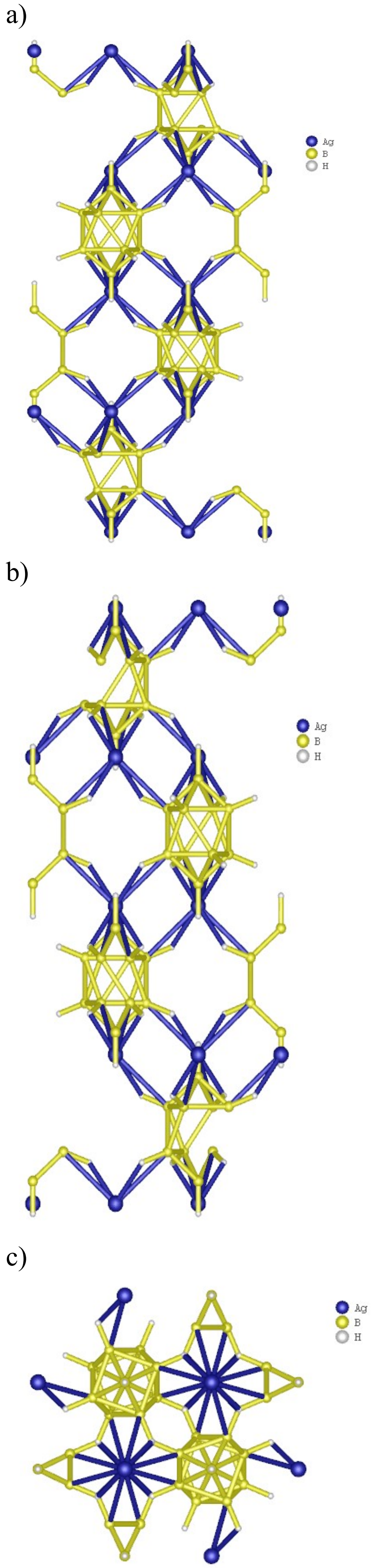

Fig. S3. Projections of the crystal structure of $Ag_2[B_{10}H_{10}]$ along 100 (a), 010 (b), and 001 (c). Data are from cif file 1790981.[S1]

Expressions used for analysis of the proton spin-lattice relaxation rates

The standard model based on Lorentzian spectral densities[S2,S3] for fluctuating dipole-dipole interactions relates the proton spin-lattice relaxation rate R_1^H with the parameters of these fluctuations. According to our estimates for the studied compounds, the "rigid-lattice" second moment of the ^{1}H NMR line is dominated by the ^{1}H – ^{1}H and ^{1}H – ^{11}B dipole-dipole interactions, while contributions due to interactions of ^{1}H with other nuclear spins can be neglected. In this case, the proton spin-lattice relaxation rate can be written as the sum of the ^{1}H – ^{1}H and ^{1}H – ^{11}B contributions:

$$\begin{aligned} R_1^H &= \frac{2\Delta M_{HH}\tau_c}{3}\left[\frac{1}{1+\omega_H^2\tau_c^2}+\frac{4}{1+4\omega_H^2\tau_c^2}\right] \\ &+ \frac{\Delta M_{HB}\tau_c}{2}\left[\frac{1}{1+(\omega_H-\omega_B)^2\tau_c^2}+\frac{3}{1+\omega_H^2\tau_c^2}+\frac{6}{1+(\omega_H+\omega_B)^2\tau_c^2}\right] \end{aligned} \tag{S1}$$

where ω_H and ω_B are the resonance frequencies of ^{1}H and ^{11}B, respectively, and ΔM_{HH} and ΔM_{HB} are the parts of the dipolar second moments due to ^{1}H – ^{1}H and ^{1}H – ^{11}B interactions that are caused to fluctuate by the reorientational process. The dipolar correlation times τ_c are simply related to the corresponding mean residence times τ between successive H jumps: $\tau_c = \tau$ for H – H and H – B interactions within the same reorienting group, and $\tau_c = \tau/2$ for the interactions between different reorienting groups; the temperature dependence of τ_i is governed by the Arrhenius relation:

$$\tau = \tau_0 \exp(E_a / k_B T) \ . \tag{S2}$$

Since each of the H – H and H – B terms in Equation (S1) exhibits nearly the same temperature and frequency dependence, it is practically impossible to determine the amplitude factors ΔM_{HH} and ΔM_{HB} *independently* from the fits to the experimental spin-lattice relaxation rate data. For the studied compounds, the estimates of the "rigid-lattice" second moments show that both the H – H and H – B contributions are of the same order of magnitude. Therefore, for the fits we have assumed that $\Delta M_{HH} = \Delta M_{HB} = \Delta M/2$.

For $Ag_2[B_{10}H_{10}]$, the experimental proton spin-relaxation data suggest the presence of a jump rate distribution, and we have used the model based on a Gaussian distribution of the activation energies.[S4] For this model, the relaxation rate is expressed as

$$R_1^H = \int R_1^H(E_a) G(E_a, \overline{E}_a, \Delta E_a) dE_a \ , \qquad \text{(S4)}$$

where $G(E_a, \overline{E}_a, \Delta E_a)$ is the Gaussian distribution centered on $\overline{E}_a$ with the dispersion ΔE_a, and $R_1^H(E_a)$ is given by equations (S1) and (S2).

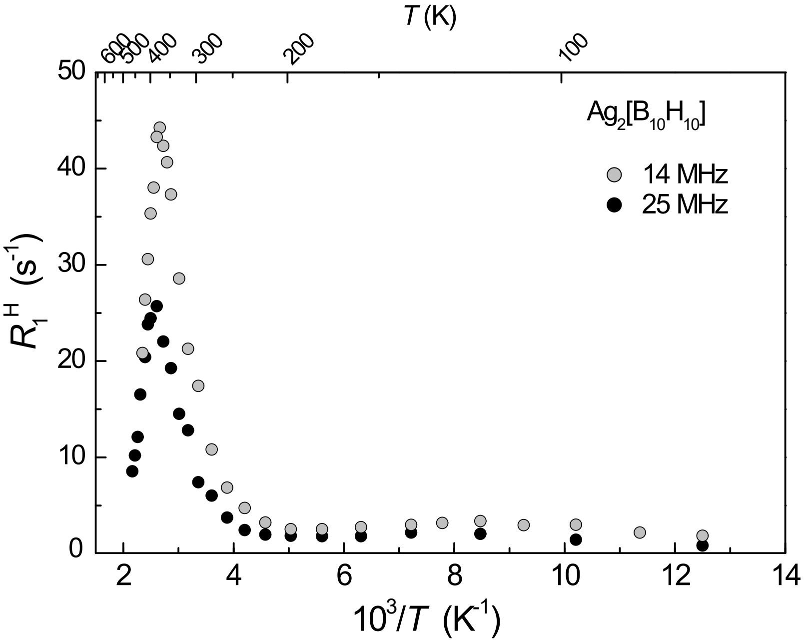

Fig. S4. Proton spin-lattice relaxation rates measured at 14 and 25 MHz for $Ag_2[B_{10}H_{10}]$ at the linear relaxation rate scale.

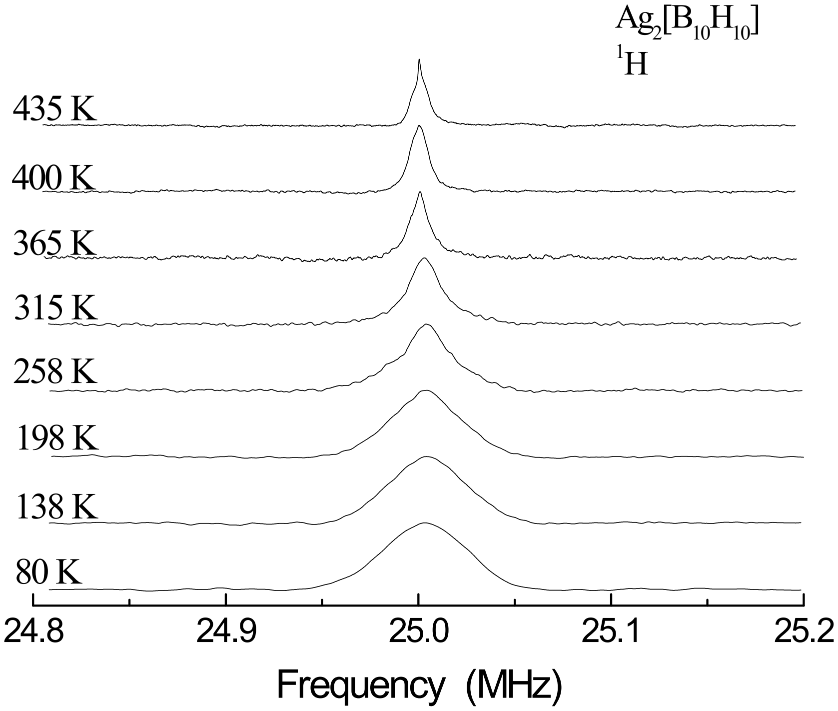

Fig. S5. Evolution of the ^1H NMR spectra with temperature.

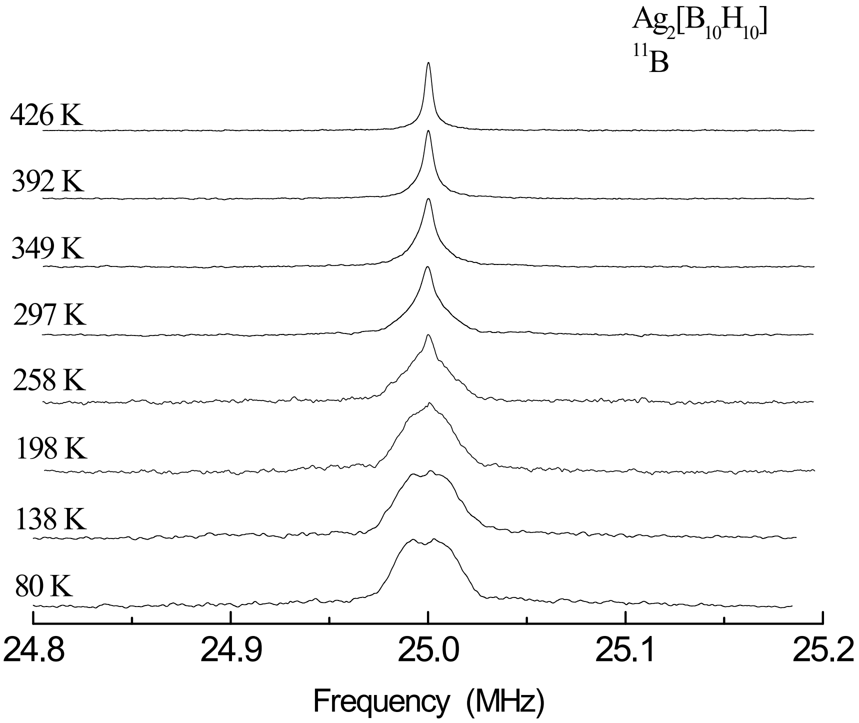

Fig. S6. Evolution of the ^{11}B NMR spectra with temperature.

Table S2. Results of the elemental analysis for $Tl_2[B_{10}H_{10}]$

Elements	H	B	Tl
Calc. (wt. %)	1.91	20.52	77.57
Exp. (wt. %)	1.89	20.48	77.51

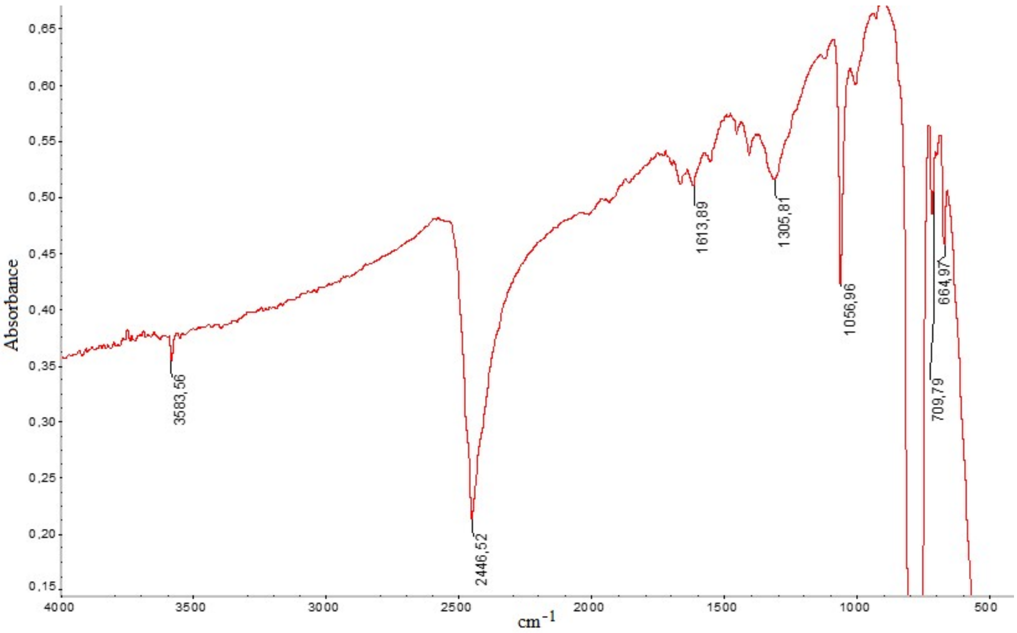

Fig. S7. IR spectrum of $Tl_2[B_{10}H_{10}]$: ν(BH) = 2446 cm^{-1}, δ(BBH) = 1057 cm^{-1}.

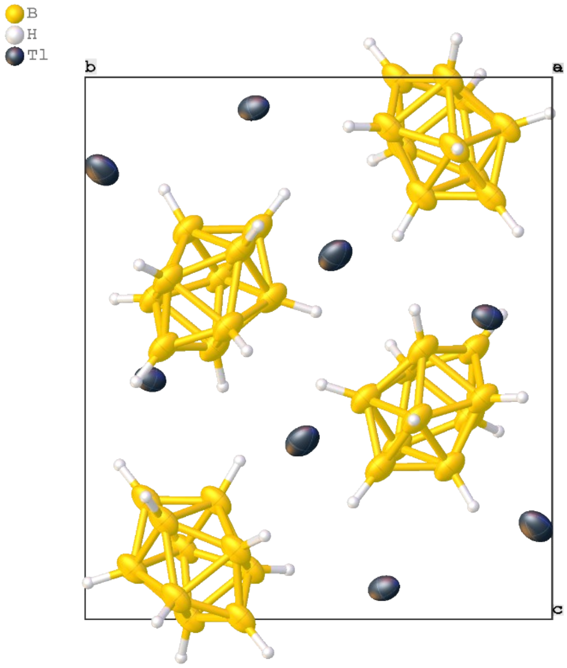

Fig. S8. Schematic view of the unit cell of $Tl_2[B_{10}H_{10}]$ along *a* axis.[S5]

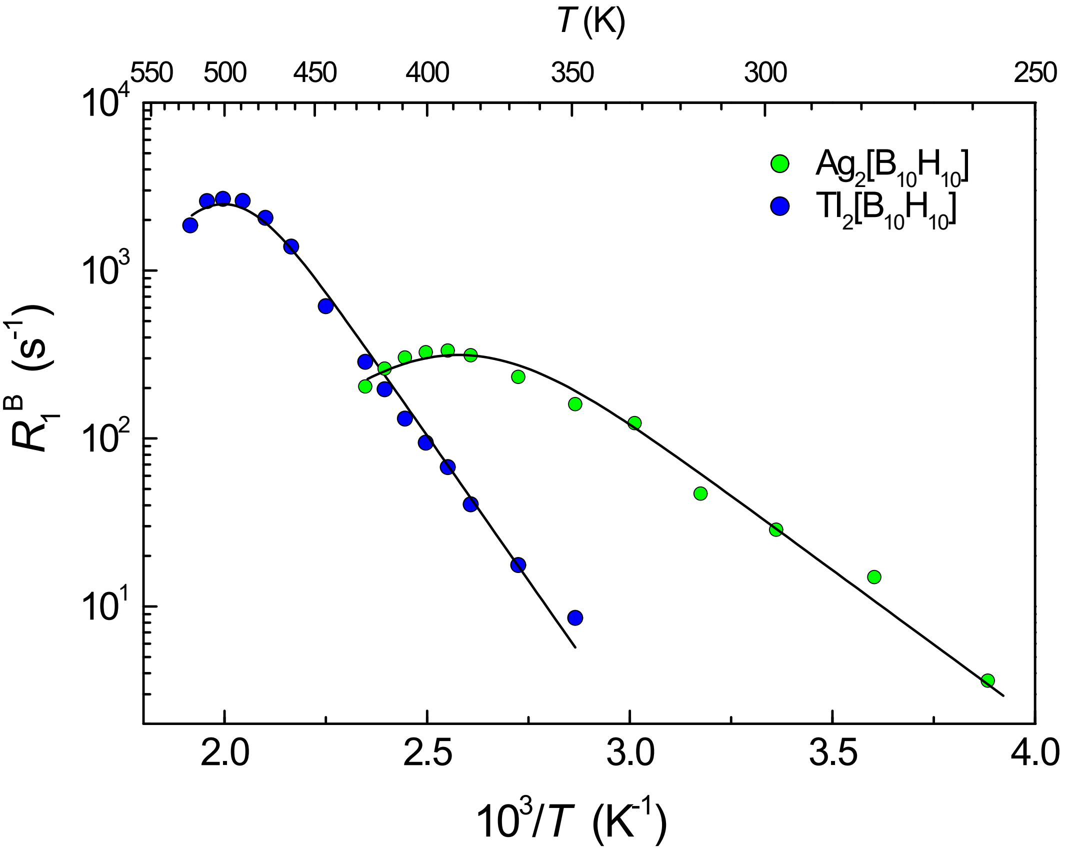

Fig. S9. Combined presentation of the ^{11}B spin-lattice relaxation rates measured at 25 MHz for both $Ag_2[B_{10}H_{10}]$ and $Tl_2[B_{10}H_{10}]$ as functions of the inverse temperature. Solid curves show the fits of the standard model to the data.

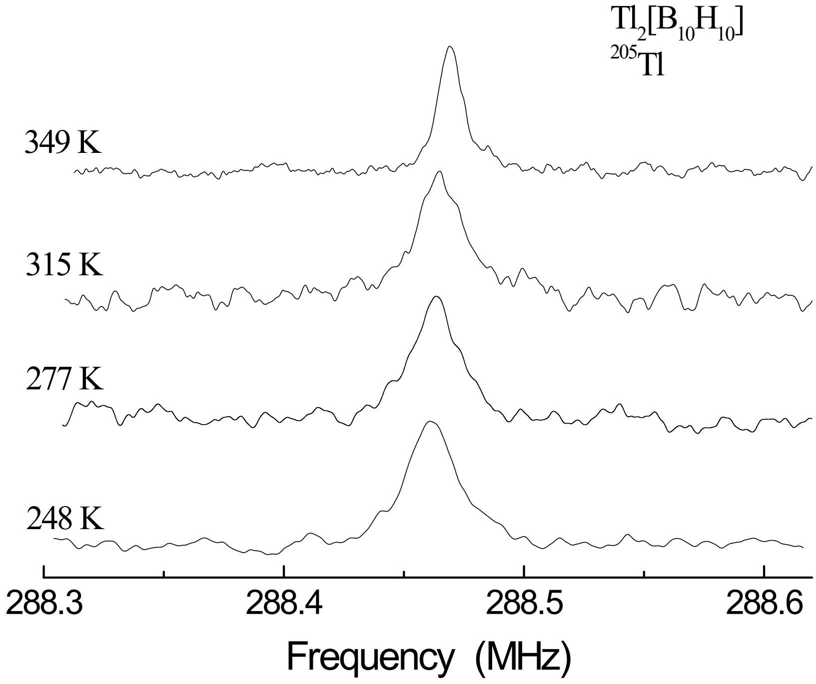

Fig. S10. Evolution of ^{205}Tl NMR spectrum for $Tl_2[B_{10}H_{10}]$ with temperature.

References

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