## **SUPPORTING INFORMATION**

# Synthesis, structure and magnetic properties of a series of Ln(III) complexes with radical-anionic iminopyridine ligands: effect of the lanthanide ion over the slow relaxation of the magnetization.

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## **Experimental Section**

**General Conditions:** All experiments were performed in evacuated tubes by standard Schlenk and glove-box techniques with the rigorous exclusion of traces of moisture and air. After drying over KOH, THF was purified by distillation from sodium/benzophenone ketyl; toluene and hexane were dried by distillation from sodium/triglyme and benzophenone ketyl before use. Anhydrous LnCl<sub>3</sub> (Ln = Tb, Dy, Er, Y, Gd),<sup>1</sup> iminopyridine (2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>)NCH(C<sub>5</sub>H<sub>4</sub>N)<sup>2</sup> and {[(2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>)NCH(C<sub>5</sub>H<sub>4</sub>N)<sup>-</sup>]K(THF)<sub>2</sub>}<sup>2</sup><sup>3</sup> were prepared according to literature procedures. All other commercially available chemicals were used after the appropriate purifications. IR spectra were recorded as Nujol mulls on a Bruker-Vertex 70 spectrophotometer. The N, C, H elemental analyses were carried out in the microanalytical laboratory of the IOMC by means of a Carlo Erba Model 1106 elemental analyser with an accepted tolerance of 0.4 unit on carbon (C), hydrogen (H), and nitrogen (N). Lanthanide metal analysis was carried out by complexonometric titration.

 $[(2,6-Pri_2C_6H_3)NCH(C_5H_4N)^{-}]_3Tb$ **Synthesis** of (1): А solution of {[(2,6- $Pr_{2}^{i}C_{6}H_{3}NCH(C_{5}H_{4}N)$  [K(THF)<sub>2</sub>]<sub>2</sub> prepared in situ from IPy (0.1944 g, 0.73 mmol) and potassium (0.0314 g, 0.8031 mmol) in THF (35 mL) was added to a suspension of TbCl<sub>3</sub> (0.0645 g, 0.24 mmol) in 10 mL of THF at 0 °C. The reaction mixture was stirred for 12 h at 25 °C, then 1 h at 60 °C, filtered and the volatiles were removed in vacuum. The dark green solid residue was extracted with  $2 \times 50$  mL of toluene. The solvent was removed in vacuum and the remaining solid was dissolved in THF (25 mL). Slow concentration of the solution at room temperature afforded 1 as dark green crystals in 75% yield (0.179 g). C<sub>56</sub>H<sub>70</sub>N<sub>6</sub>O<sub>0.50</sub>Tb (994.10): calc. C 67.66, H 7.10, N 8.45, Tb 15.99; found C 67.31, H 7.44, N 8.59, Tb 16.37. IR (Nujol, KBr): v = 3056 (m), 1645 (s), 1588 (m), 1571 (s), 1535 (s), 1509 (s), 1399 (s), 1318 (s), 1273 (s), 1253 (s), 1152 (s), 1109 (s), 991 (s), 904 (s), 799 (s), 757 (s), 737 (s), 625 (s), 537 (s), 504 (s) cm<sup>-1</sup>.

**Synthesis** of  $[(2,6-Pri_2C_6H_3)NCH(C_5H_4N)^{-}]_3Dy$ (2): А solution of {[(2,6- $Pr_{2}^{i}C_{6}H_{3}NCH(C_{5}H_{4}N)$  [K(THF)<sub>2</sub>]<sub>2</sub> prepared in situ from IPy (0.202 g, 0.76 mmol) and potassium (0.032 g, 0.82 mmol) in THF (35 mL) was added to a suspension of DyCl<sub>3</sub> (0.0680 g, 0.253 mmol) in 10 mL of THF at 0 °C. The reaction mixture was stirred for 1 h at 60 °C, filtered and the volatiles were removed in vacuum. The dark green solid residue was extracted with 2×40 mL of toluene. The solvent was removed in vacuum and the remaining solid was dissolved in THF/toluene mixture (10/1). Slow concentration of the solution at room temperature afforded 2 as dark green crystals in 72% yield (0.184 g). C<sub>57,50</sub>H<sub>70</sub>N<sub>6</sub>Dy (1007.69): calc. C 68.53, H 7.00, N 8.34, Dy 16.13; found C 68.19, H 7.37, N 8.05, Dy 16.50. IR (Nujol, KBr): v = 3056 (s), 1645 (s), 1588 (s), 1571 (s), 1535 (s), 1509 (s), 1402 (s), 1318 (s), 1273 (s), 1169 (s), 1152 (s), 1109 (s), 994 (s), 904 (s), 799 (s), 757 (s), 737 (s), 625 (s), 537 (s), 504 (s) cm<sup>-1</sup>.

Synthesis of  $[(2,6-\text{Pri}_2\text{C}_6\text{H}_3)\text{NCH}(\text{C}_5\text{H}_4\text{N})^{-}]_3\text{Er}$  (3): A solution of  $\{[(2,6-\text{Pri}_2\text{C}_6\text{H}_3)\text{NCH}(\text{C}_5\text{H}_4\text{N})^{-}]\text{K}(\text{THF})_2\}_2$  prepared in situ from IPy (0.3142 g, 1.18 mmol) and potassium (0.0508 g, 1.30 mmol) in THF (35 mL) was added to a suspension of  $\text{ErCl}_3$  (0.1076 g, 0.393 mmol) in 10 mL of THF at 0 °C. The reaction mixture was stirred for 12 h at 25 °C, then 1 h at 60 °C, filtered and the volatiles were removed in vacuum. The dark green solid residue was extracted with 3×50 mL of toluene. The solvent was removed in vacuum and the remaining solid was dissolved in THF/toluene

mixture (10/1). Slow concentration of the solution at room temperature afforded **3** as dark green crystals in 70% yield (0.279 g).  $C_{57.50}H_{70}N_6$ Er (1012.45): calc. C 68.21, H 6.97, N 8.30, Er 16.52; found C 67.85, H 7.12, N 8.07, Er 16.13. IR (Nujol, KBr): v = 3059 (s), 1642 (s), 1589 (s), 1569 (s), 1535 (s), 1510 (s), 1403 (s), 1318 (s), 1273 (s), 1254 (s), 1152 (s), 1109 (s), 994 (s), 904 (s), 800 (s), 758 (s), 738 (s), 625 (s), 538 (s), 504 (s) cm<sup>-1</sup>.

**Synthesis** of  $[(2,6-Pri_2C_6H_3)NCH(C_5H_4N)^{-}]_3Y$ (4): solution А of {[(2,6- $Pr_{2}^{i}C_{6}H_{3}NCH(C_{5}H_{4}N)$  [K(THF)<sub>2</sub>}<sub>2</sub> prepared in situ from IPy (0.349 g, 1.31 mmol) and potassium (0.060 g, 1.53 mmol) in THF (35 mL) was added to a suspension of YCl<sub>3</sub> (0.0856 g, 0.438 mmol) in 10 mL of THF at 0 °C. The reaction mixture was stirred for 12 h at 25 °C, then 6 h at 60 °C, filtered and the volatiles were removed in vacuum. The dark green solid residue was extracted with 3×50 mL of toluene. The solvent was removed in vacuum and the remaining solid was dissolved in THF/toluene mixture (10/1). Slow concentration of the solution at room temperature afforded 4 as dark green crystals in 73% yield (0.291 g). C<sub>57.50</sub>H<sub>70</sub>N<sub>6</sub>Y (934.10): calc. C 73.93, H 7.55, N 9.00, Y 9.52; found C 73.58, H 7.81, N 8.73, Y 9.20. IR (Nujol, KBr): v = 3059 (m), 1656 (s), 1600 (s), 1569 (s), 1539 (s), 1508 (s), 1403 (s), 1319 (s), 1272 (s), 1253 (s), 1153 (s), 1108 (s), 994 (s), 905 (s), 802 (s), 761 (s), 736 (s), 625 (s), 541 (s), 502 (s)  $cm^{-1}$ .

 $[(2,6-Pri_2C_6H_3)NCH(C_5H_4N)^{-}]_3Gd$ **Synthesis** of (5): solution {[(2,6-А of Pri<sub>2</sub>C<sub>6</sub>H<sub>3</sub>)NCH(C<sub>5</sub>H<sub>4</sub>N)<sup>-</sup>]K(THF)<sub>22</sub> prepared in situ from IPy (0.310 g, 1.164 mmol) and potassium (0.050 g, 1.279 mmol) in THF (35 mL) was added to a suspension of GdCl<sub>3</sub> (0.1023 g, 0.388 mmol) in 10 mL of THF at 0 °C. The reaction mixture was stirred for 12 h at 25 °C, then 6 h at 60 °C, filtered and the volatiles were removed in vacuum. The dark green solid residue was extracted with 4×50 mL of toluene. The solvent was removed in vacuum and the remaining solid was dissolved in THF/toluene mixture (10/1). Slow concentration of the solution at room temperature afforded 5 as dark green crystals in 71% yield (0.291 g). C<sub>57.50</sub>H<sub>70</sub>N<sub>6</sub>Gd (1002.44): calc. C 68.89, H 7.04, N 8.38, Gd 15.69; found C 68.56, H 7.29, N 8.15, Gd 15.43. IR (Nujol, KBr): v = 3059 (m), 1645 (s), 1589 (s), 1569 (s), 1535 (s), 1507 (s), 1403 (s), 1318 (s), 1276 (s), 1251 (s), 1152 (s), 1110 (s), 992 (s), 904 (s), 800 (s), 758 (s), 738 (s), 625 (s), 538 (s), 504 (s) cm<sup>-1</sup>.

#### X-Ray crystallography.

The X-ray data for 1–5 were collected on *Bruker Smart Apex II* (1, T = 120K), *Bruker D8 Quest* (2, 4, 5, T = 100 K) and *Agilent Xcalibur* (3, T = 100 K) diffractometers (*MoK<sub>a</sub>*-radiation,  $\omega$ -scans technique,  $\lambda = 0.71073$  Å) using *APEX3<sup>5</sup>* and *CrysAlis Pro<sup>6</sup>* software packages. The structures were solved by dual-space methods and were refined by full-matrix least squares on  $F^2$  for all data using *SHELX<sup>7</sup>*. *SADABS*<sup>8</sup> and *CrysAlis Pro* were used to perform area-detector scaling and absorption corrections. All non-hydrogen atoms were found from Fourier syntheses of electron density and were refined anisotropically (except 2,6-isopropylphenyl substituents in 1, which were disordered in two sites and were refined isotropically). Hydrogen atoms in 1–5 were placed in calculated positions and were refined in the "riding" model with  $U(H)_{iso} = 1.2U_{eq}$  of their parent atoms ( $U(H)_{iso} = 1.5U_{eq}$  for methyl groups). Unresolved THF molecules in 1 were removed by the *SQUEEZE*<sup>9</sup> method. The crystallographic data and structure refinement details for 1–5 are given in Table S1. CCDC–1883465 (1), 1883466 (2), 1883467 (3), 1883468 (4) and 1926051 (5) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre: ccdc.cam.ac.uk/structures.

#### **EPR Measurements**

X-band EPR spectra were recorded on Bruker EMX (working frequency ~9.7 GHz) spectrometer. The  $g_i$  values were determined using DPPH as the reference ( $g_i = 2.0037$ ).

#### Magnetic Measurements.

Magnetic susceptibility data were collected with a Quantum Design MPMS-XL SQUID magnetometer working in the range 1.8–350 K with the magnetic field up to 7 Tesla. The sample were prepared in a glove box. The data were corrected for the sample holder and the diamagnetic contributions calculated from the Pascal's constants. The AC magnetic susceptibility measurements were carried out in the presence of a 3 Oe oscillating field in zero or applied external DC field.

## **DC Magnetic properties**

The direct current (dc) magnetic properties of the compounds 1–5 were investigated by using a SQUID MPMS-XL magnetometer in the 1.8 – 300 K temperature range. The temperature dependences of  $\chi T$  could be seen in Fig. S3 left. At room temperature, the experimental  $\chi T$  values of 11.69, 14.00 and 12.23 cm<sup>3</sup>.K.mol<sup>-1</sup> for 1, 2 and 3, respectively, are slightly lower than the theoretical values of 12.94, 15.30 and 12.60 expected for a non-interacting Ln<sup>3+</sup> ion (Tb<sup>3+</sup> C = 11.82 cm<sup>3</sup>.K.mol<sup>-1</sup>;  $Dy^{3+} C = 14.17$  cm<sup>3</sup>.K.mol<sup>-1</sup>;  $Er^{3+} C = 11.48$  cm<sup>3</sup>.K.mol<sup>-1</sup>) and three radical ligands (S = 1/2, C = 0.375 cm<sup>3</sup>.K.mol<sup>-1</sup>). Such features could be rationalized by the occurrence of predominant antiferromagnetic interactions, which are still operative at room temperature as frequently observed in other lanthanide/radical examples.<sup>1-3</sup> However, the occurrence of radical/radical exchange interactions has also should be considered,<sup>4</sup> as suggested by EPR studies. Moreover, we cannot exclude that this fact may be due to the presence of crystallographic disorder in ligands and/or solvents, which induces the distribution of different species in samples.

Hence, further insights into the lanthanide/radical and radical/radical interactions could be obtained by the study of 4 and 5. At room temperature the yttrium analogue 4 exhibits a  $\chi T$  value of 1.160 cm<sup>3</sup>.K.mol<sup>-1</sup>, which is in good agreement with the value of 1.125 cm<sup>3</sup>.K.mol<sup>-1</sup> expected for three independent radicals. Diminishing the temperature results in a gradual decrease of  $\chi T$ , with a kind of plateau between 75 and 25 K and then a drop of  $\chi T$  below 20 K to reach the value of 0.116 cm<sup>3</sup>.K.mol<sup>-1</sup> at 1.8 K, reflecting predominant antiferromagnetic interactions. The triangular arrangement of the radials might suggest the occurrence of spin frustration. However, the S-like shape of this curve is much less pronounced in comparison to that observed for classical frustrated triangle systems such as tricopper triangular systems (S =  $\frac{1}{2}$ ). This suggests that not only the presence of strong intratrimer antiferromagnetic interactions, but also intermolecular ones have to be considered.<sup>5-6</sup> This is further confirmed by the  $\gamma T$  behavior at low temperature, where the experimental  $\gamma T$  value is below the theoretical Curie law one (only the ground spin or degenerated spin doublets should be thermally populated in equilateral triangles at low temperature). This hypothesis is not surprising regarding the short intermolecular contacts between the radicals (C-C distances of 3.676 Å), which are comparable to the intramolecular ones. Moreover, attempts to fit the  $\chi T vs T$  curves with an isotropic Hamiltonian with  $J_{12} = J_{13} = J_{23}$  (with the PHI software<sup>7</sup>) event including the intermolecular interactions to extract the exchange interactions was not successful.

As regards 5, the room temperature  $\chi T$  of 10.44 cm<sup>3</sup>.K.mol<sup>-1</sup> is slightly larger than the expected value of 9.00 cm<sup>3</sup>.K.mol<sup>-1</sup> for non-interacting three radicals and one gadolinium ion ( $C = 7.88 \text{ cm}^3.\text{K.mol}^{-1}$ ). Further information about the lanthanide-radical exchange interaction could be obtained thanks to the absence of spin-orbit coupling for the gadolinium ion. Thus, the thermal dependence of  $\chi T$  could be modeled with the PHI software<sup>7</sup> by considering three Gd<sup>3+</sup> (S = 7/2) -radical ( $S = \frac{1}{2}$ ) and three radical-radical exchange interactions (see Scheme 1), plus an intermolecular *zJ* term. The best obtained fit parameters obtained by fitting both the temperature dependence and the field dependence of the susceptibility and are:  $J_{\text{Gd-rad}} = -0.84 \pm 0.04 \text{ cm}^{-1}$ ;  $J_{\text{rad-rad}} = -42 \pm 4 \text{ cm}^{-1}$ ;  $zJ = -0.060 \pm 0.002 \text{ cm}^{-1}$  and  $g = 2.149 \pm 0.006$ . The magnetization at 1.8 K under a 70 kOe is equal to 7.00 N $\beta$ , which is exactly equal to the value expected for a single Gd<sup>3+</sup> ion. However, the field dependence of the magnetization at low field is not superimposed on a Brillouin function.

For compounds 1-3 a decrease of  $\chi T$  is observed upon cooling, reflecting the inherent thermal depopulation of the  $\pm m_J$  levels from the Ln<sup>3+</sup> ions possibly associated with the antiferromagnetic interactions to reach the values of 3.34, 5.55 and 3.23 cm<sup>3</sup>.K.mol<sup>-1</sup> at 1.8 K for compounds 1, 2 and 3 respectively. The field dependence of the magnetization does not exhibit a clear saturation indicating the presence of a magnetic anisotropy for complexes 1-3 (Fig. S4 right).



Scheme S1: Exchange coupling scheme for 4 (left) and 5 (right).



Figure S1: Perspective view of the crystal packing for 2 along the *c* crystallographic axis. Hydrogen atoms have been omitted for clarity.



Figure S2. The X-band EPR spectrum of 4 in solid-state at room temperature.



**Figure S3:** Left: temperature dependence of  $\chi T$  under an applied magnetic field of 1000 Oe for **1-3**. The red solid line represents the fit for **5** using the PHI software.<sup>7</sup> Right: field dependence of the magnetization at 1.8 K for **1-5**. The dashed line represents the fit of **5** with a Brillouin function (S = 7/2, g = 2.00) while the solid line accounts to the fit obtained with PHI.<sup>7</sup>



**Figure S4.** Temperature dependence of  $\chi'$  and  $\chi''$  for **2** for different frequencies.



**Figure S5:** Cole-Cole (Argand) plots obtained using the ac susceptibility data for **2** (0 Oe). The solid lines correspond to the best fit obtained with a generalized Debye model.



Figure S6. Field dependence of the relaxation time for 2 at 15 K.



**Figure S7.** Frequency dependence of  $\chi'$  and  $\chi''$  for **2** under a 1000 Oe dc field.



**Figure S8:** Cole-Cole (Argand) plot obtained using the ac susceptibility data for **2** (1000 Oe) The solid lines correspond to the best fit obtained with a generalized Debye model.



**Figure S9.** Frequency dependence of  $\chi'$  and  $\chi''$  under various dc fields for **1**.



**Figure S10.** Frequency dependence of  $\chi'$  and  $\chi''$  under various dc fields for **3**.

				*	
	1	2	3	4	5
Empirical formula	C54H66N6Tb,	C54H66N6Dy,	C54H66N6Er,	C <sub>54</sub> H <sub>66</sub> N <sub>6</sub> Y,	C54H66N6Gd,
	<sup>1</sup> / <sub>2</sub> C <sub>4</sub> H <sub>8</sub> O	<sup>1</sup> / <sub>2</sub> C <sub>7</sub> H <sub>8</sub>			
Formula Weight	994.10	1007.69	1012.45	934.10	1002.44
Crystal System	Trigonal	Trigonal	Trigonal	Trigonal	Trigonal
Space Group	R-3	R-3	R-3	R-3	R-3
<i>a</i> , Å	18.519(3)	18.6116(5)	18.5889(3)	18.6899(7)	18.6764(14)
<i>b</i> , Å	18.519(3)	18.6116(5)	18.5889(3)	18.6899(7)	18.6764(14)
<i>c</i> , Å	25.112(5)	25.2890(7)	25.4010(7)	25.1795(10)	25.337(2)
α, °	90	90	90	90	90
β, °	90	90	90	90	90
γ, °	120	120	120	120	120
V, Å <sup>3</sup>	7459(3)	7586.3(5)	7601.3(3)	7617.1(6)	7653.7(13)
Z	6	6	6	6	6
$d_{calc}$ , Mg/m <sup>3</sup>	1.280	1.323	1.327	1.222	1.305
$\mu$ , mm <sup>-1</sup>	1.462	1.520	1.699	1.191	1.342
F(000)	2982	3138	3150	2976	3126
Crystal Size, mm	0.32×0.23×0.21	0.18×0.15×0.10	0.30×0.23×0.19	0.30×0.20×0.20	0.15×0.15×0.05
$\theta$ Range for Data	2.06-28.00	2.42-30.14	3.00-27.09	2.05-26.11	2.41-28.72
Collection, °					
Index Ranges	$-23 \le h \le 24$	$-26 \le h \le 26$	$-23 \le h \le 23$	$-23 \le h \le 23$	$-25 \le h \le 25$
	$-24 \le k \le 22$	$-26 \le k \le 26$	$-23 \le k \le 23$	$-23 \le k \le 23$	$-25 \le k \le 25$
	$-33 \le l \le 26$	$-35 \le l \le 35$	$-32 \le l \le 32$	$-31 \le l \le 31$	$-34 \le l \le 34$
Reflns Collected	14651	36732	35624	33567	35561
Independent	4009 (0.0863)	4968 (0.0303)	3725 (0.0270)	3349 (0.0324)	4396 (0.0295)
Reflns (R <sub>int</sub> )					
Completeness to	99.9	99.8	99.8	99.8	99.8
θ, %					
Data / Restraints /	4009 / 26 / 163	4968 / 189 / 283	3725 / 99 / 228	3349 / 287 / 331	4396 / 99 / 228
Parameters					
$S(F^2)$	1.006	1.051	1.015	1.080	1.008
Final R Indices (I	$R_1 = 0.0435$	$R_1 = 0.0269$	$R_1 = 0.0217$	$R_1 = 0.0383$	$R_1 = 0.0275$
$> 2\sigma(I))$	$R_2 = 0.0752$	$R_2 = 0.0602$	$R_2 = 0.0534$	$R_2 = 0.1026$	$R_2 = 0.0640$
R Indices (all	$R_I = 0.0726$	$R_I = 0.0352$	$R_I = 0.0287$	$R_I = 0.0400$	$R_I = 0.0353$
data)	$R_2 = 0.0838$	$R_2 = 0.0643$	$R_2 = 0.0576$	$R_2 = 0.1037$	$R_2 = 0.0694$
Largest Diff. Peak	0.71 / -1.05	1.06 / -1.63	0.58 / -0.27	1.63 / -0.67	1.53 / -1.71
and Hole, e/Å <sup>3</sup>					

 Table S1. The crystal data and structures refinement details for complexes 1–5.

	HP	РРҮ	OC	TPR	JPPY
1	24.183	26.425	4.088	15.034	28.587
2	24.276	26.445	3.988	15.136	28.586
3	22.751	25.721	3.954	16.198	27.868
4	24.469	26.504	3.975	15.028	28.694
5	24.177	26.450	4.280	15.037	28.562
		PPY: I O	HP: Hexagon Pentagonal Pyramic C: Octahedron	1	

 Table S2.
 SHAPE analysis for compounds 1-5

TPR: Trigonal Prism JPPY: Johnson Pentagonal Pyramid

Table S3. Fitting of the	he Cole-Cole plots	with a gene	eralized Debye	model for	temperature
ranging from 2 to 25 K	under a zero dc fiel	d for <b>2</b> .			

<i>T</i> (K)	$\chi_S$ (cm <sup>3</sup> . mol <sup>-1</sup> )	$\chi_T$ (cm <sup>3</sup> . mol <sup>-1</sup> )	α
2	2.20658	2.90418	0.42757
5	1.36096	1.6082	0.3343
8	1.01329	1.125	0.06522
11	0.79387	0.9051	0.22715
12	0.7404	0.83955	0.20602
13.6	0.67561	0.76176	0.16236
14	0.65208	0.74829	0.23611
15	0.62001	0.70705	0.20045
16	0.58845	0.67014	0.19242
16.8	0.57001	0.64149	0.13387
17	0.5612	0.63729	0.18743
18	0.53176	0.60789	0.21552
18.4	0.52351	0.59465	0.15807
20	0.48507	0.554	0.1522
21	0.47038	0.53209	0.13035
22	0.45714	0.51117	0.08153
23	0.43192	0.49152	0.12435

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24	0.41148	0.47465	0.14592
25	0.39194	0.45667	0.12132

**Table S4**. Fitting of the Cole-Cole plots with a generalized Debye model for temperature ranging from 2 to 18.58 K under a 1000 Oe dc field for **2**.

<i>T</i> (K)	$\chi_S$ (cm <sup>3</sup> . mol <sup>-1</sup> )	$\chi_T$ (cm <sup>3</sup> . mol <sup>-1</sup> )	α
2	1.75092	3.29421	0.76163
4	1.43013	1.97195	0.65224
6	1.17606	1.44489	0.46463
8	0.97802	1.15704	0.372
10	0.83724	0.97543	0.33786
11.5	0.75501	0.87377	0.294
12.92	0.69076	0.79613	0.29626
14.35	0.63631	0.73142	0.29739
15.75	0.59241	0.67775	0.25532
17.16	0.55219	0.63139	0.26566
18.58	0.51715	0.59022	0.21186

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