

**Dalton Transactions Paper Ref.: B709901K (Revised)**

**Co(II) and Co(III) complexes of thioether-containing  
hexadentate pyrazine amide ligands: C–S bond cleavage and  
cyclometallation reaction**

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**Supporting Information**

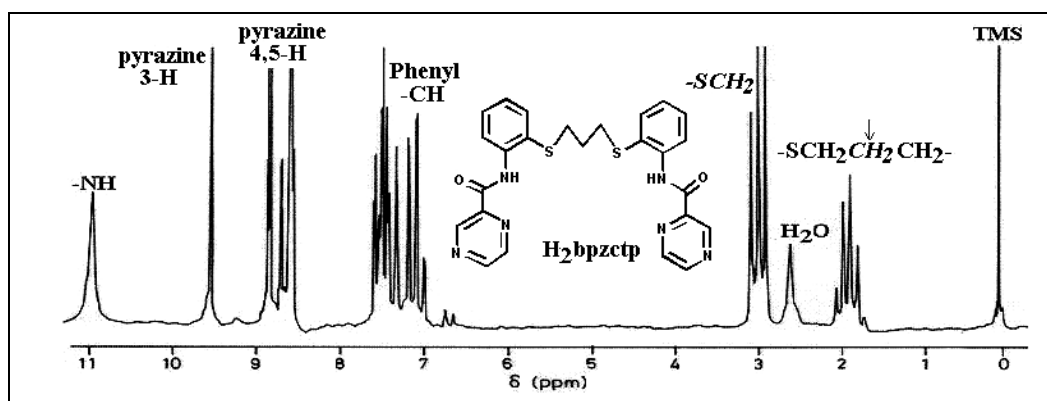


Fig. S1.  $^1\text{H}$  NMR spectrum (80 MHz;  $\text{CDCl}_3$ ; standard  $\text{SiMe}_4$ ; 300 K) of  $\text{H}_2\text{L}^2$ .

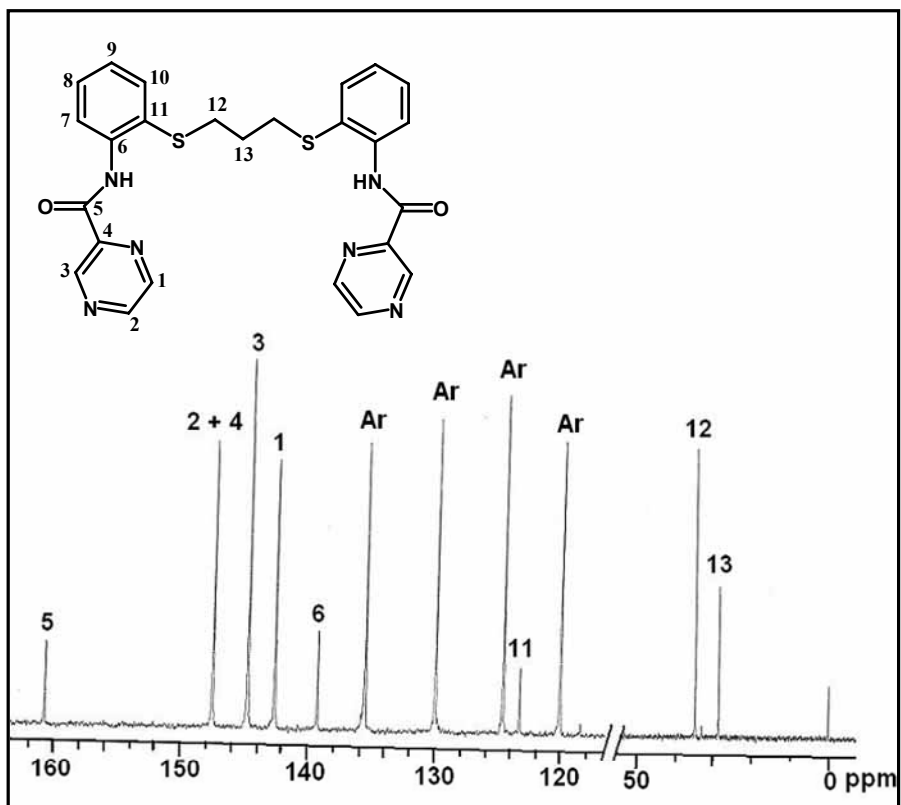
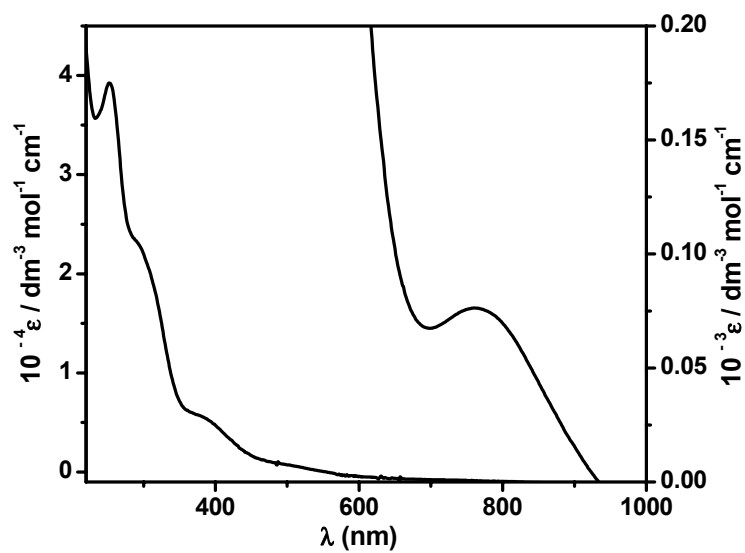


Fig. 2.  $^{13}C$  NMR spectrum (400 MHz;  $CDCl_3$ ; standard  $SiMe_4$ ; 300 K) of  $H_2L^2$ .

(a)



(b)

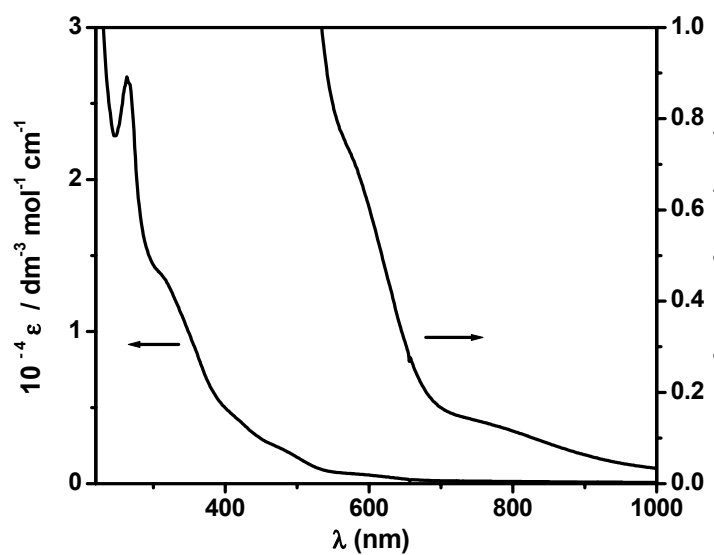
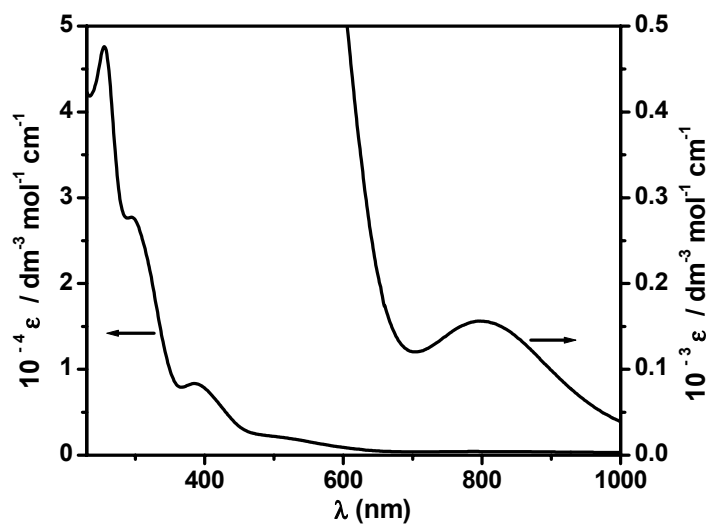


Fig. S3. UV-VIS spectra of (a)  $[\text{Co}^{\text{II}}(\text{L}^1)]\cdot\text{MeOH}$  (**1a**) and (b)  $[\text{Co}^{\text{II}}(\text{L}^2)]\cdot\text{MeOH}$  (**1b**·MeOH) in MeCN.

(a)



(b)

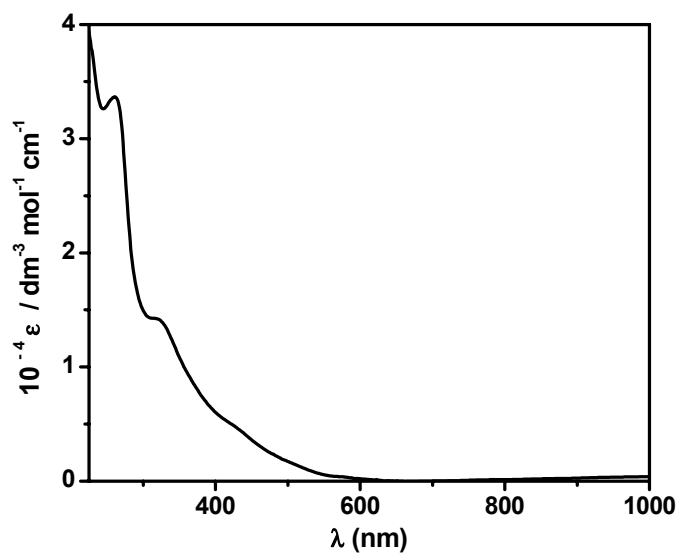


Fig. S4. UV-VIS spectra of (a)  $[\text{Co}^{\text{III}}(\text{L}^{3\text{a}})(\text{L}^{3\text{b}})]2\text{MeOH}$  (**2a**) and (b)  $[\text{Co}^{\text{III}}(\text{L}^2)][\text{ClO}_4]$  (**2b**) in MeCN

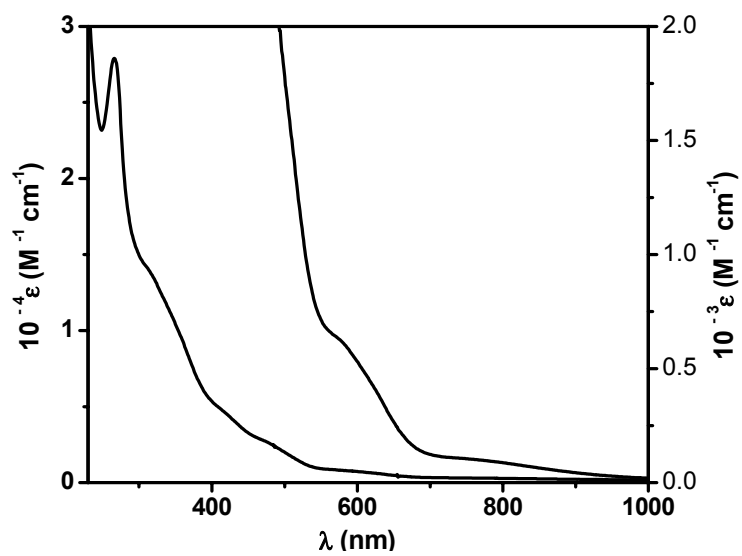


Fig. S5. UV-VIS spectra of  $[\text{Co}^{\text{III}}(\text{L}^{2n})]$  (**3**) in  $\text{CH}_2\text{Cl}_2$ .

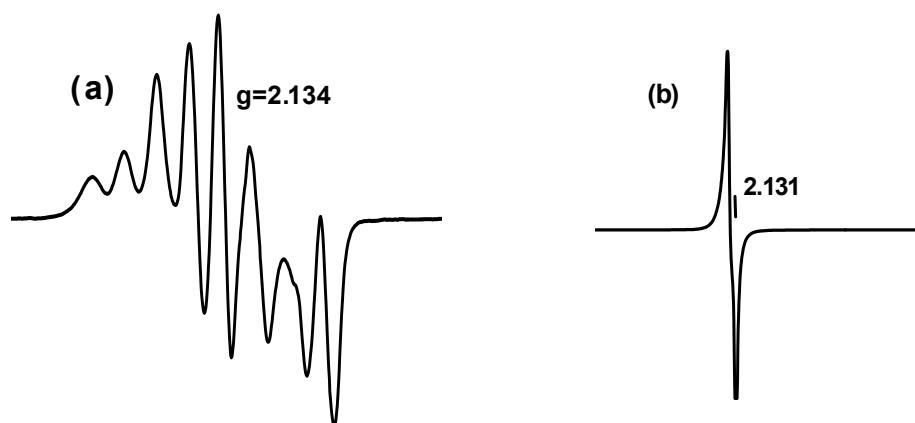


Fig. S6. EPR spectra of  $[\text{Co}^{\text{II}}(\text{L}^2)]^*\text{MeOH}$  (**1b**\*MeOH): (a) MeCN- $\text{C}_6\text{H}_5\text{CH}_3$  glass (1:1) and (b) polycrystalline sample at 120 K.

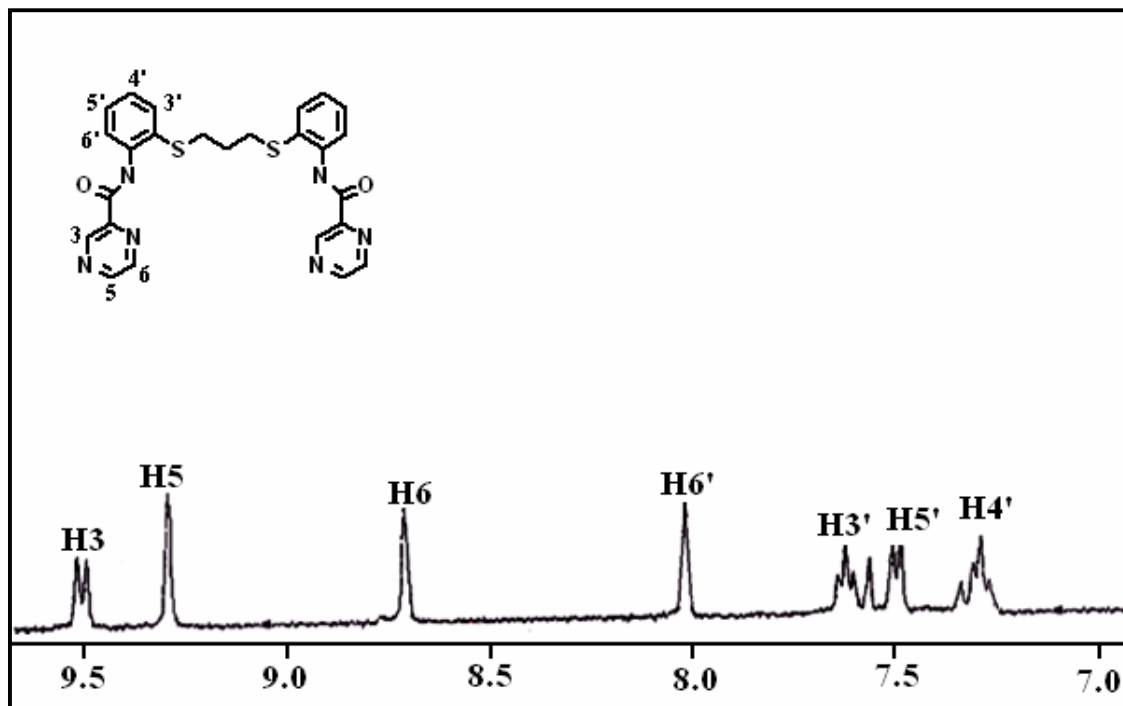


Fig. S7. <sup>1</sup>H NMR spectrum (400 MHz; CD<sub>3</sub>CN; standard SiMe<sub>4</sub>; 300 K) of selected portion of [Co<sup>III</sup>(L<sup>2</sup>)] [ClO<sub>4</sub>] (**2b**).

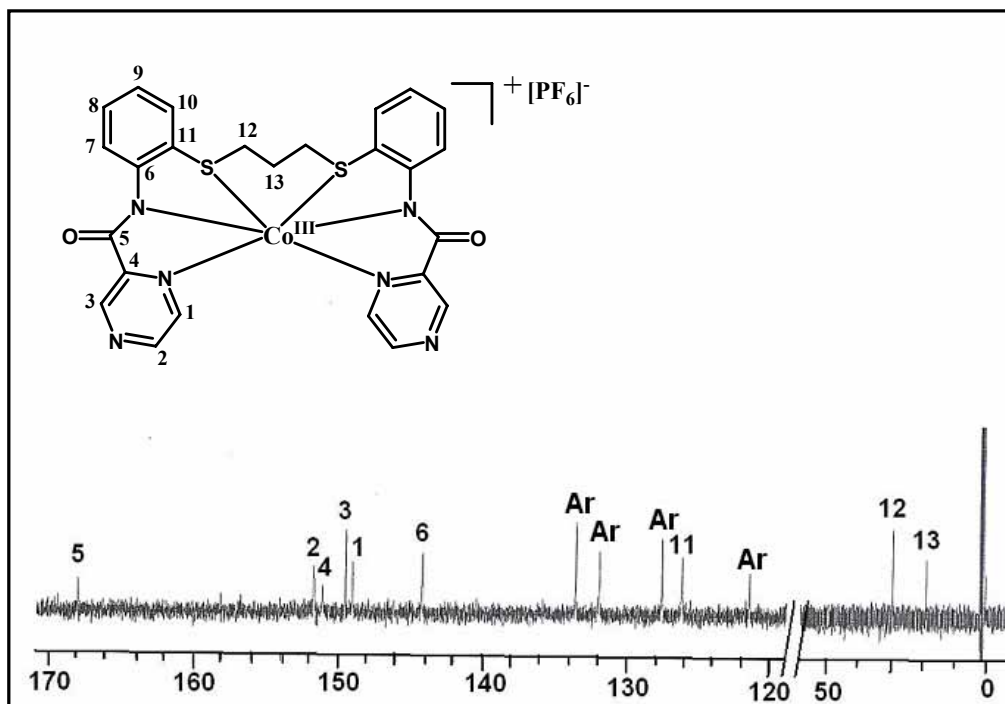


Fig. S8. <sup>13</sup>C NMR spectrum (400 MHz; CD<sub>3</sub>CN; standard SiMe<sub>4</sub>; 300 K) of **2c**. The δ<sub>C</sub> values: 19.910, 29.330, 121.490, 126.221, 127.595, 131.930, 133.543, 144.172, 149.034, 149.503, 151.091, 151.692, 168.014.

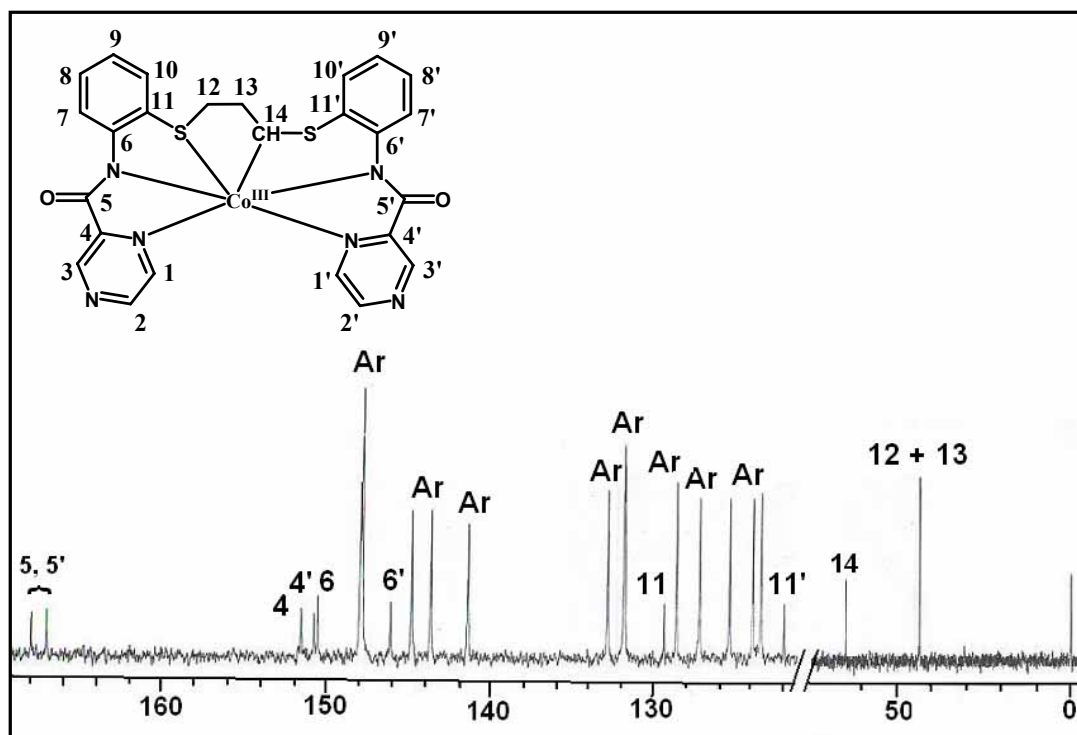


Fig. S9.  $^{13}\text{C}$  NMR spectrum (400 MHz;  $\text{CDCl}_3$ ; standard  $\text{SiMe}_4$ ; 300 K) of **3**. The  $\delta_{\text{C}}$  values: 43.242, 43.538, 64.081, 121.942, 123.341, 123.851, 125.299, 127.142, 128.582, 129.363, 131.766, 131.823, 132.810, 141.457, 143.728, 144.896, 146.138, 147.866, 147.973, 150.532, 150.770, 151.560, 167.085, 168.014.



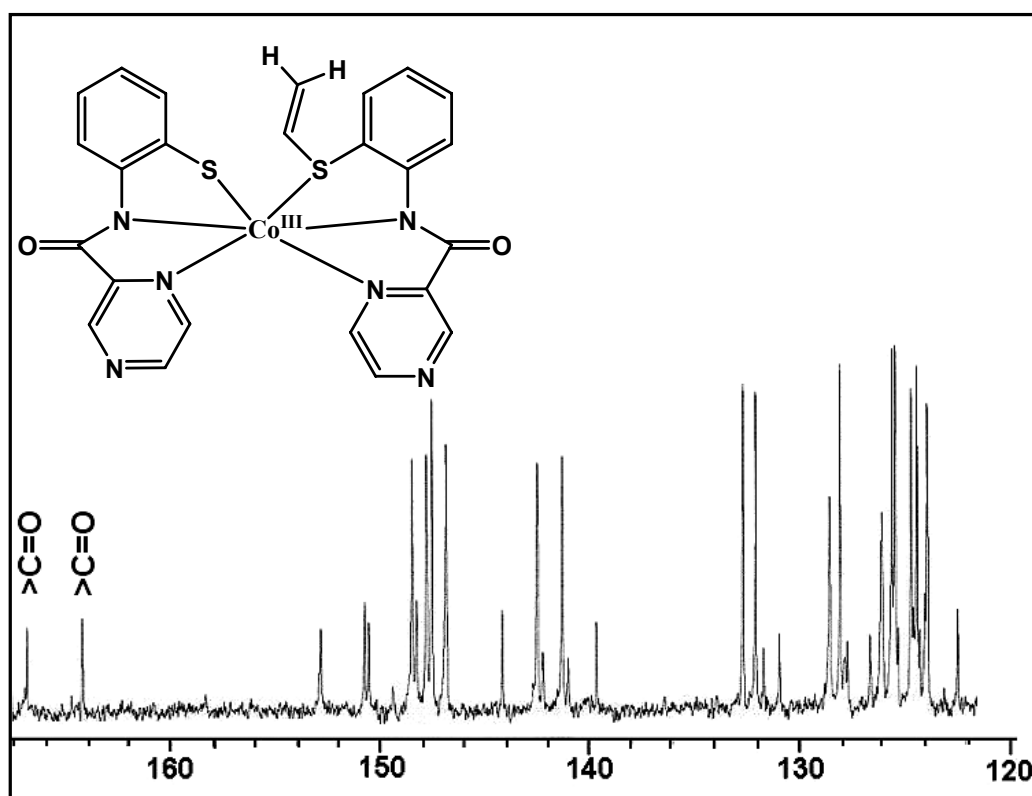


Fig. S10. <sup>13</sup>C NMR spectrum (400 MHz; CD<sub>3</sub>CN; standard SiMe<sub>4</sub>; 300 K) of **2a**. The  $\delta_C$  values: 122.403, 123.859, 124.361, 124.624, 125.373, 125.513, 126.007, 128.014, 128.516, 132.029, 132.638, 139.655, 141.317, 142.477, 144.164, 146.813, 147.521, 147.800, 148.475, 150.532, 150.721, 152.819, 164.238, 166.895.