

Supporting Information

for

**First Systematic Investigation of C-H ... Cl Hydrogen Bonding Using
Inorganic Supramolecular Synthons: Lamellar, Stitched Stair-Case,
Linked-Ladder, and Helical Structures**

By

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Figure S1. ^1H NMR spectrum (400 MHz) of $[(\text{L}^2)\text{CoCl}_2]$ (**1**) in CD_3COCD_3 (only relevant portion is shown). Assignments are indicated.

Figure S2. ^1H NMR spectrum (400 MHz) of $[(\text{L}^1)\text{ZnCl}_2]$ (**4**) in $(\text{CD}_3)_2\text{SO}$ (only relevant portion is shown). Assignments are indicated.

Figure S3. ^1H NMR spectrum (400 MHz) of $[(\text{L}^3)\text{ZnCl}_2]$ (**5**) in $(\text{CD}_3)_2\text{SO}$ (only relevant portion is shown). Assignments are indicated.

Figure S4. ^1H NMR spectrum (400 MHz) of $[(\text{L}^5)\text{ZnCl}_2]$ (**6**) in $(\text{CD}_3)_2\text{SO}$ (only relevant portion is shown; NMe signal (not shown) appears at 3.55 δ). Assignments are indicated.

Figure S5. X-ray structure of $[(\text{L}^2)\text{CoCl}_2]$ (**1**); selected bond lengths [\AA] and angles [$^\circ$]: Co-N(1) 2.049(2), Co-N(3) 2.002(2), Co-Cl(1) 2.2249(12), Co-Cl(2) 2.2194(14), N(1)-Co-N(3) 92.64(9) $^\circ$, N(1)-Co-Cl(1) 107.70(7) $^\circ$, N(1)-Co-Cl(2) 111.50(7) $^\circ$, N(3)-Co-Cl(1) 115.56(7) $^\circ$, N(3)-Co-Cl(2) 111.01(7) $^\circ$, Cl(1)-Co-Cl(2) 115.94(4) $^\circ$.

Figure S6. View of lamellar structure with two different alternate channels present in the solid-state structure of $[(\text{L}^2)\text{CoCl}_2]$ (**1**). All the hydrogen atoms except those involved in hydrogen bonding have been omitted for clarity.

Figure S7. A perspective view of $[(\text{L}^4)\text{CuCl}_2]$ (**3**) showing the presence of intramolecular C-H ... Cl hydrogen bonds. Hydrogen bonding parameters: $D - \text{H} \dots A$: C6 - H6A ... Cl; H ... A: 2.666 \AA ; $D \dots A$: 3.380 \AA ; $D - \text{H} \dots A$: 130.80 $^\circ$.

Figure S8. X-ray structure of $[(\text{L}^1)\text{ZnCl}_2]$ (**4**); selected bond lengths [\AA] and angles [$^\circ$]: Zn-N(1) 2.066(8), Zn-N(3) 2.045(7), Zn-Cl(1) 2.193(3), Zn-Cl(2) 2.222(3), N(1)-Zn-N(3) 91.0(3) $^\circ$, N(1)-Zn-Cl(1) 110.4(2) $^\circ$, N(1)-Zn-Cl(2) 110.1(2) $^\circ$, N(3)-Zn-Cl(1) 114.1(2) $^\circ$, N(3)-Zn-Cl(2) 110.9(2) $^\circ$, Cl(1)-Zn-Cl(2) 117.31(11) $^\circ$.

Figure S9. X-ray structure of $[(\text{L}^3)\text{ZnCl}_2]$ (**5**); selected bond lengths [\AA] and angles [$^\circ$]: Zn-N(1) 2.058(3), Zn-N(3) 2.499(3), Zn-N(5) 2.067(3), Zn-Cl(1) 2.3727(13), Zn-Cl(2) 2.2247(13), N(1)-Zn-N(3) 81.38(12) $^\circ$, N(1)-Zn-N(5) 113.95(13) $^\circ$, N(1)-Zn-Cl(1) 94.31(10) $^\circ$, N(1)-Zn-Cl(2) 118.69(10) $^\circ$, N(3)-Zn-N(5) 79.79(12) $^\circ$, N(3)-Zn-Cl(1) 167.64(7) $^\circ$, N(3)-Zn-Cl(2) 88.68(8) $^\circ$, N(5)-Zn-Cl(1) 91.54(10) $^\circ$, N(5)-Zn-Cl(2) 123.42(9) $^\circ$, Cl(1)-Zn-Cl(2) 103.50(5) $^\circ$.

Figure S10. X-ray structure of $[(\text{L}^5)\text{ZnCl}_2]$ (**6**); selected bond lengths [\AA] and angles [$^\circ$]: Zn-N(1) 2.242(8), Zn-N(2) 2.157(8), Zn-N(3) 2.232(8), Zn-Cl(1) 2.271(2), Zn-Cl(2) 2.270(2), N(1)-Zn-N(2) 86.9(4) $^\circ$, N(1)-Zn-N(3) 162.9(3) $^\circ$, N(1)-Zn-Cl(1) 97.8(2) $^\circ$, N(1)-Zn-Cl(2)

91.9(2)^o, N(2)-Zn-N(3) 77.1(4)^o, N(2)-Zn-Cl(1) 114.3(2)^o, N(2)-Zn-Cl(2) 124.4(2)^o, N(3)-Zn-Cl(1) 94.3(2)^o, N(3)-Zn-Cl(2) 92.3(2)^o, Cl(1)-Zn-Cl(2) 120.89(10)^o.

Figure S11. X-ray structure of [(bpc)CoCl₂] (bpc = bis(picolylamino)cyclohexane), showing intramolecular C-H ... Cl hydrogen bonding interactions (ref.29). All the hydrogen atoms except those involved in hydrogen bonding have been omitted for clarity. Hydrogen bonding parameters: *D* – H ... *A*ⁱ: C16 – H16A ... Cl1; H ... *A*: 2.898 Å; *D* ... *A*: 3.479 Å; *D* – H ... *A*: 121.81^o. Symmetry codes: (i) - x, y, 1/2 – z.

Figure S12. Crystal packing diagram of [(Me-Bz-dpa)CoCl₂] (Me-Bz-dpa = dipicolyamine, pyridine ring 6-substituents: Me, aliphatic amine N has Bz substituent), showing C-H ... Cl hydrogen bonding interactions (ref. 29). All the hydrogen atoms except those involved in hydrogen bonding have been omitted for clarity. Hydrogen bonding parameters: *D* – H ... *A*: C54 – H54 ... Cl2 ; H ... *A*ⁱ: 3.048Å; *D* ... *A*: 3.763 Å; *D* – H ... *A*: 136.36^o. *D* – H ... *A*: C57 – H57A ... Cl1 ; H ... *A*: 2.831 Å; *D* ... *A*: 3.530 Å; *D* – H ... *A*: 143.32^o. *D* – H ... *A*: C67 – H67C ... Cl1 ; H ... *A*: 2.860 Å; *D* ... *A*: 3.512 Å; *D* – H ... *A*: 138.48^o. Symmetry codes: (i) – 1 + x, y, z.

Figure S1

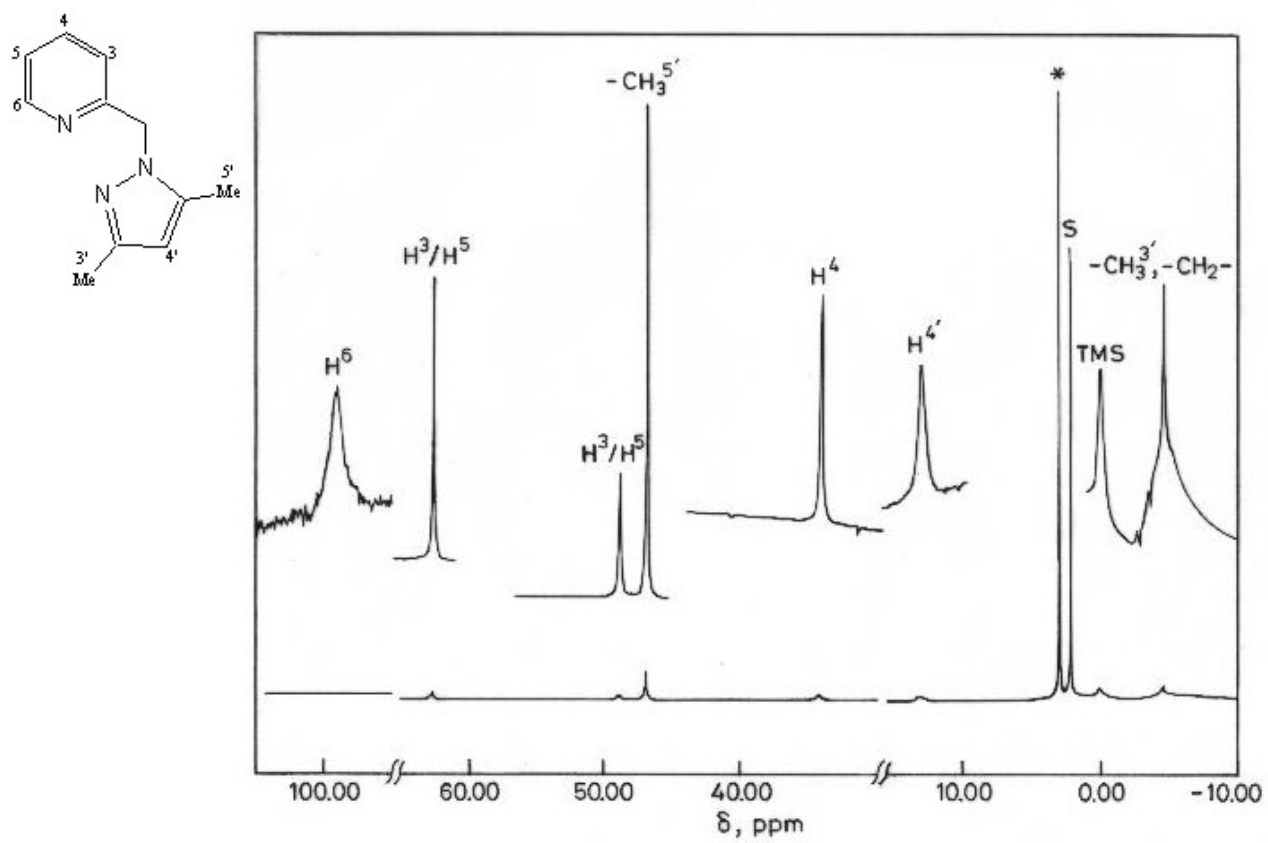


Figure S2

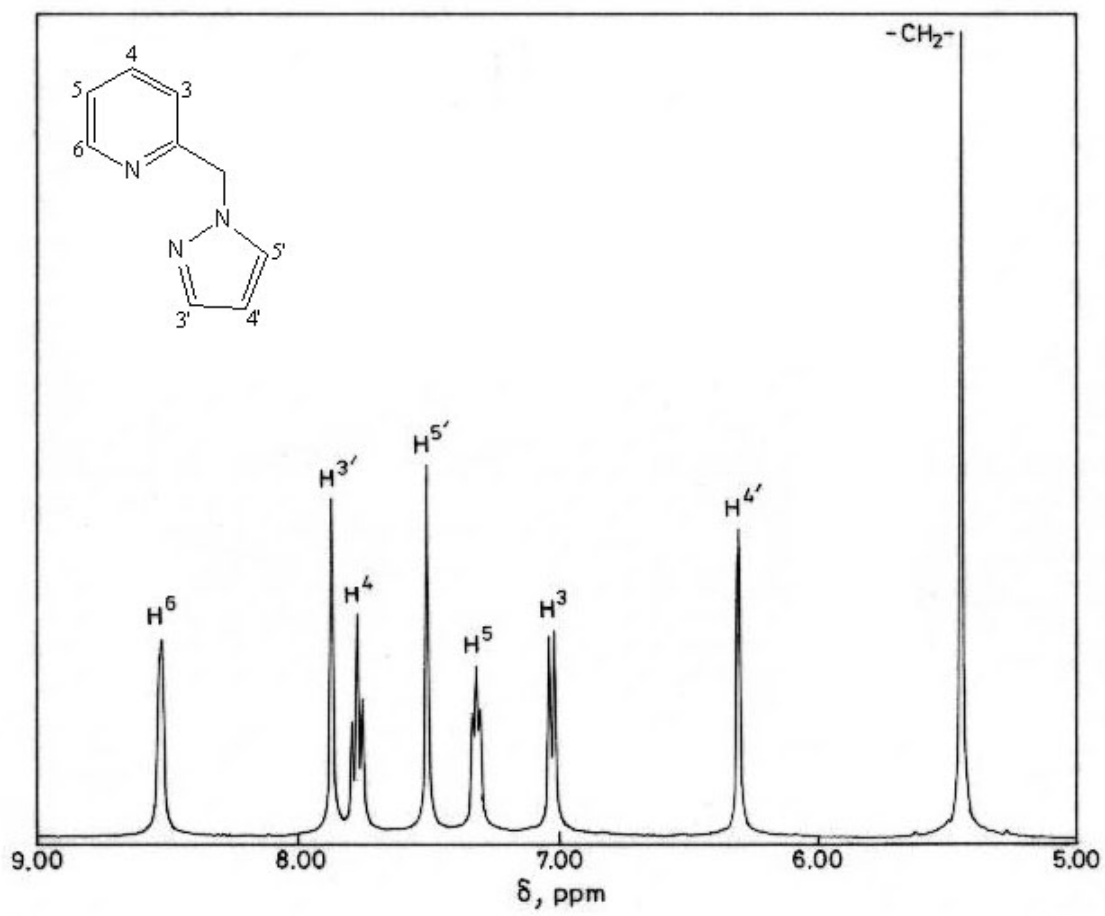


Figure S3

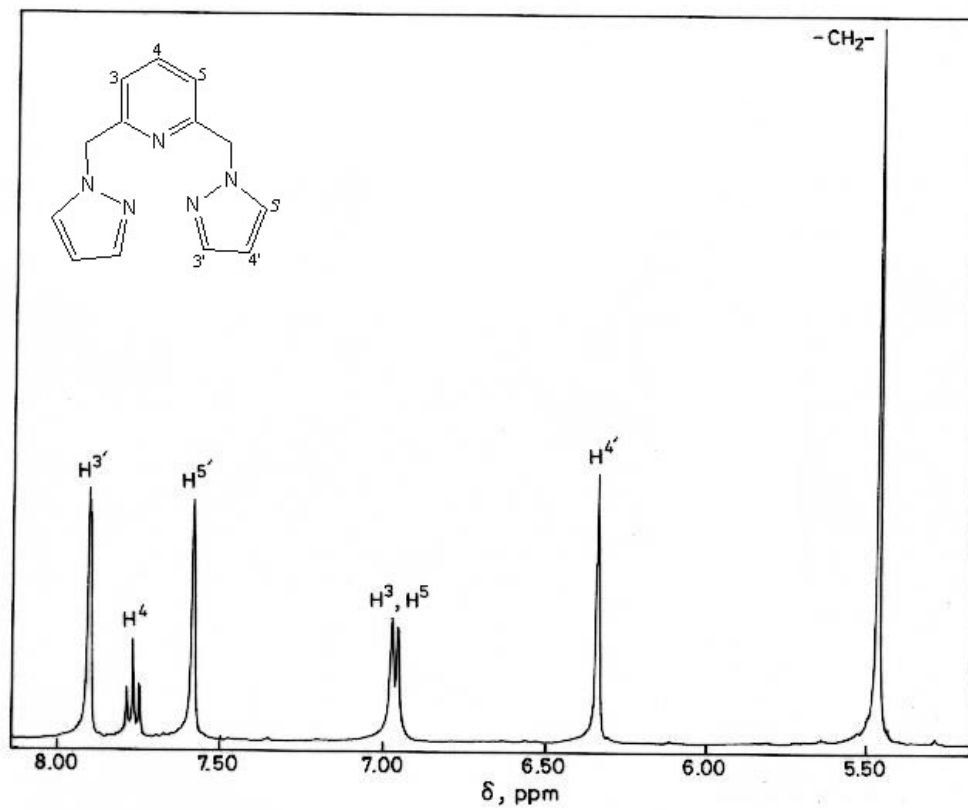


Figure S4

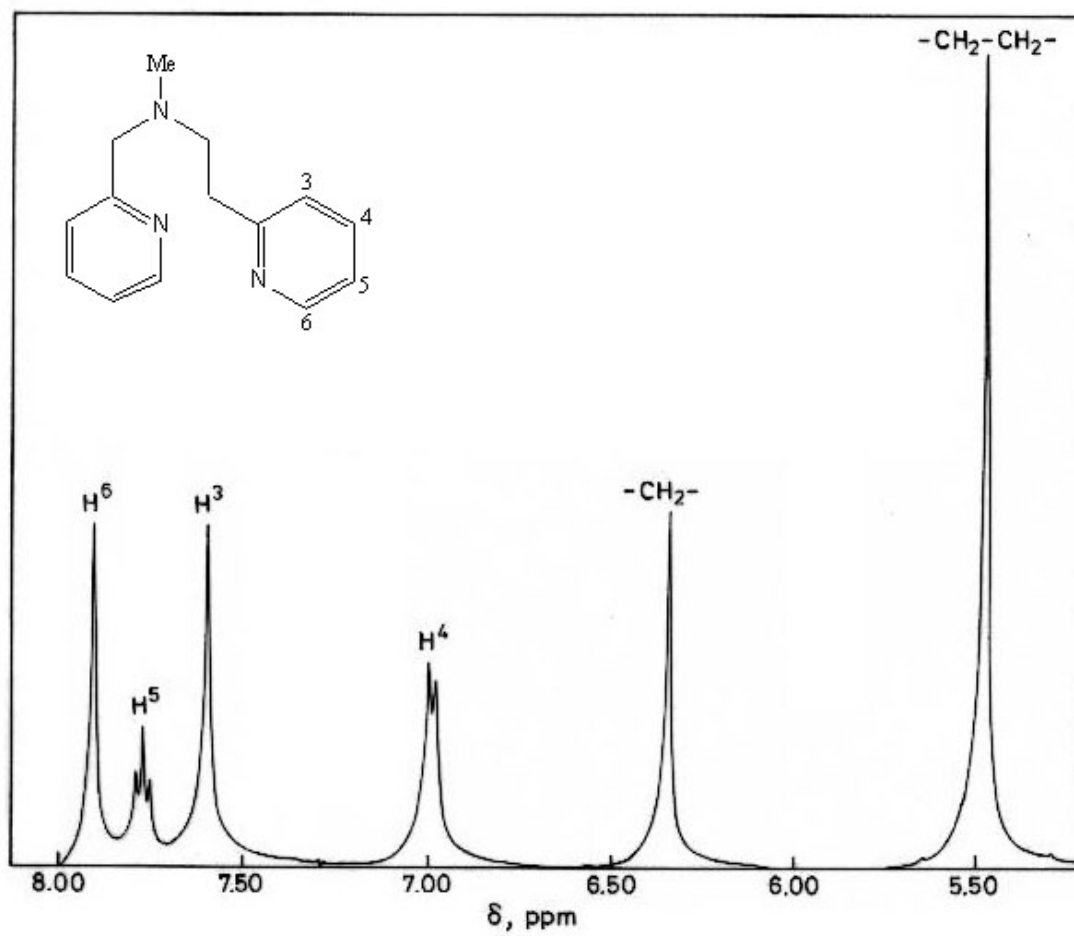


Figure S5

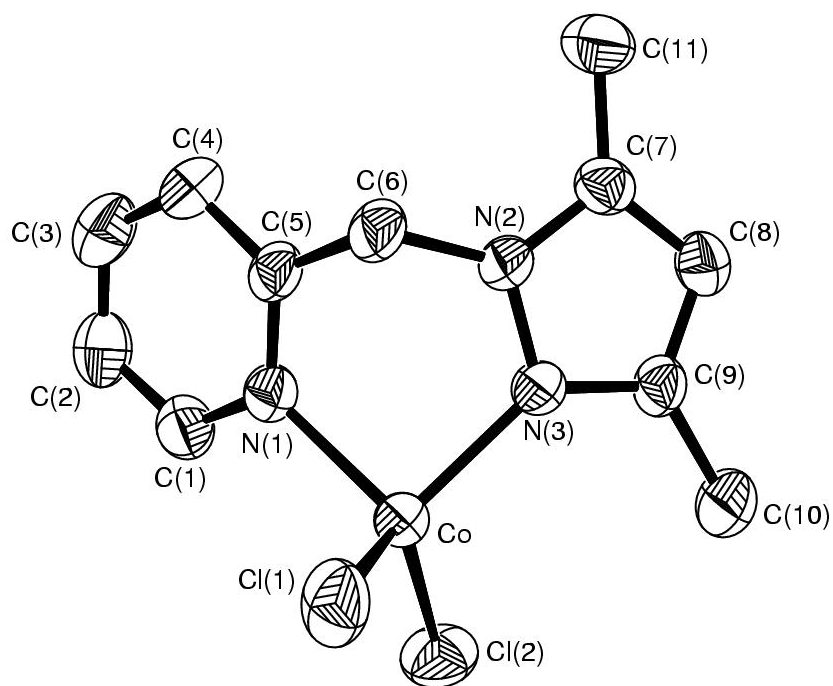


Figure S6

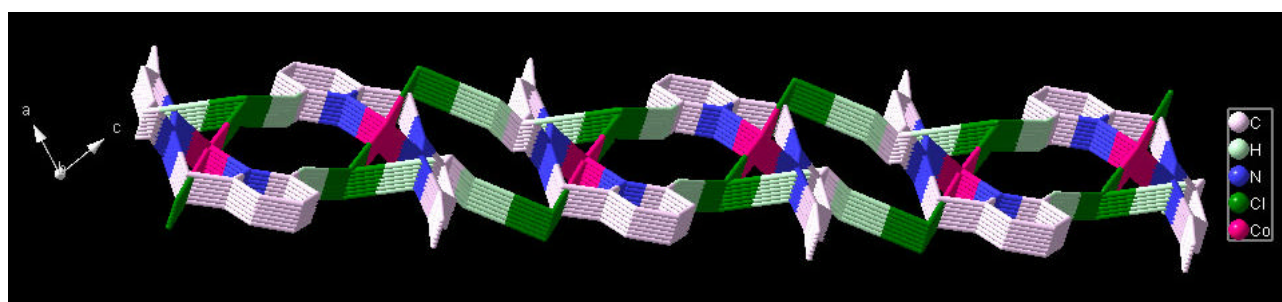


Figure S7

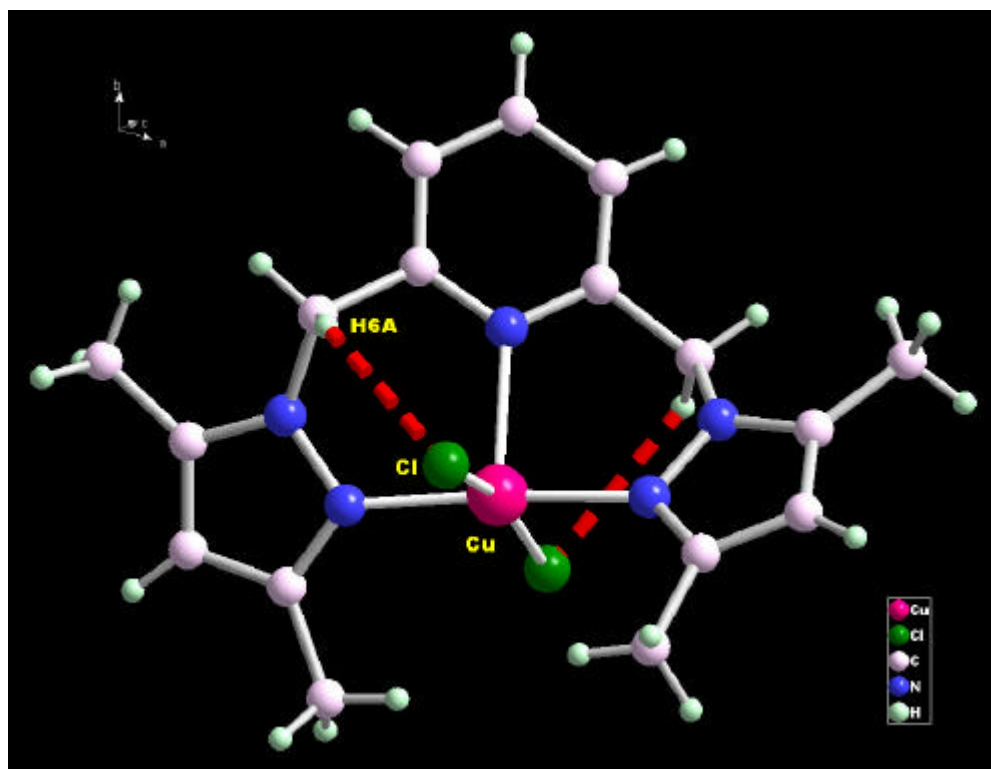


Figure S8

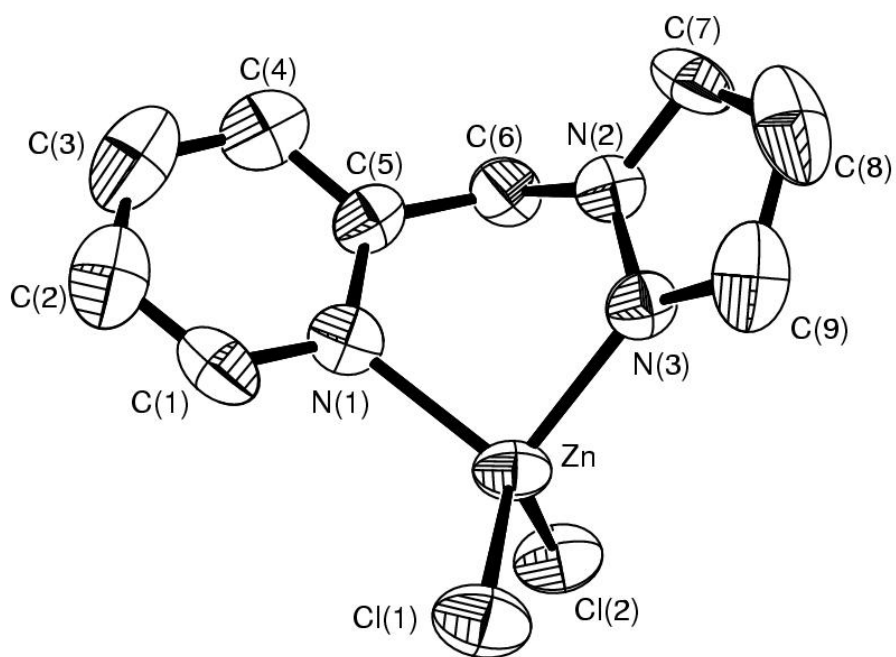


Figure S9

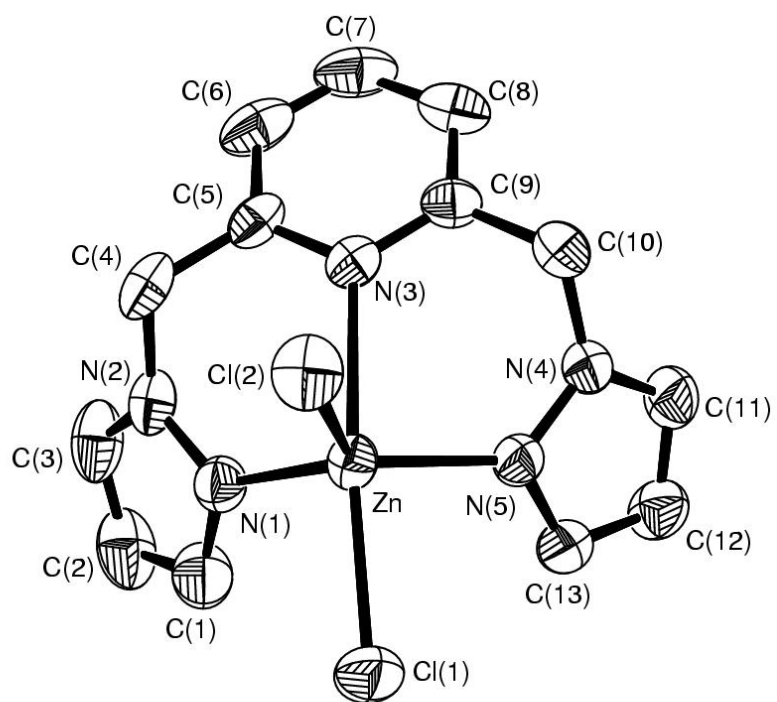


Figure S10

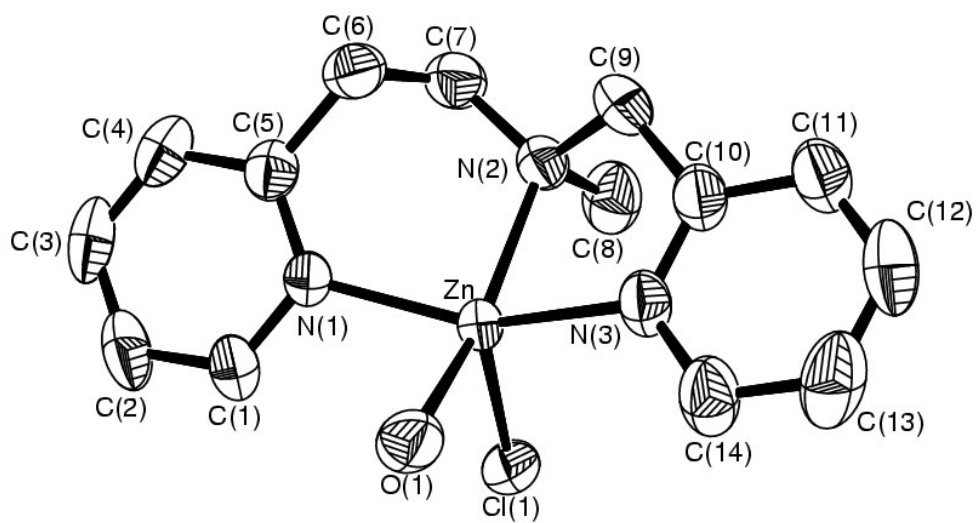


Figure S11

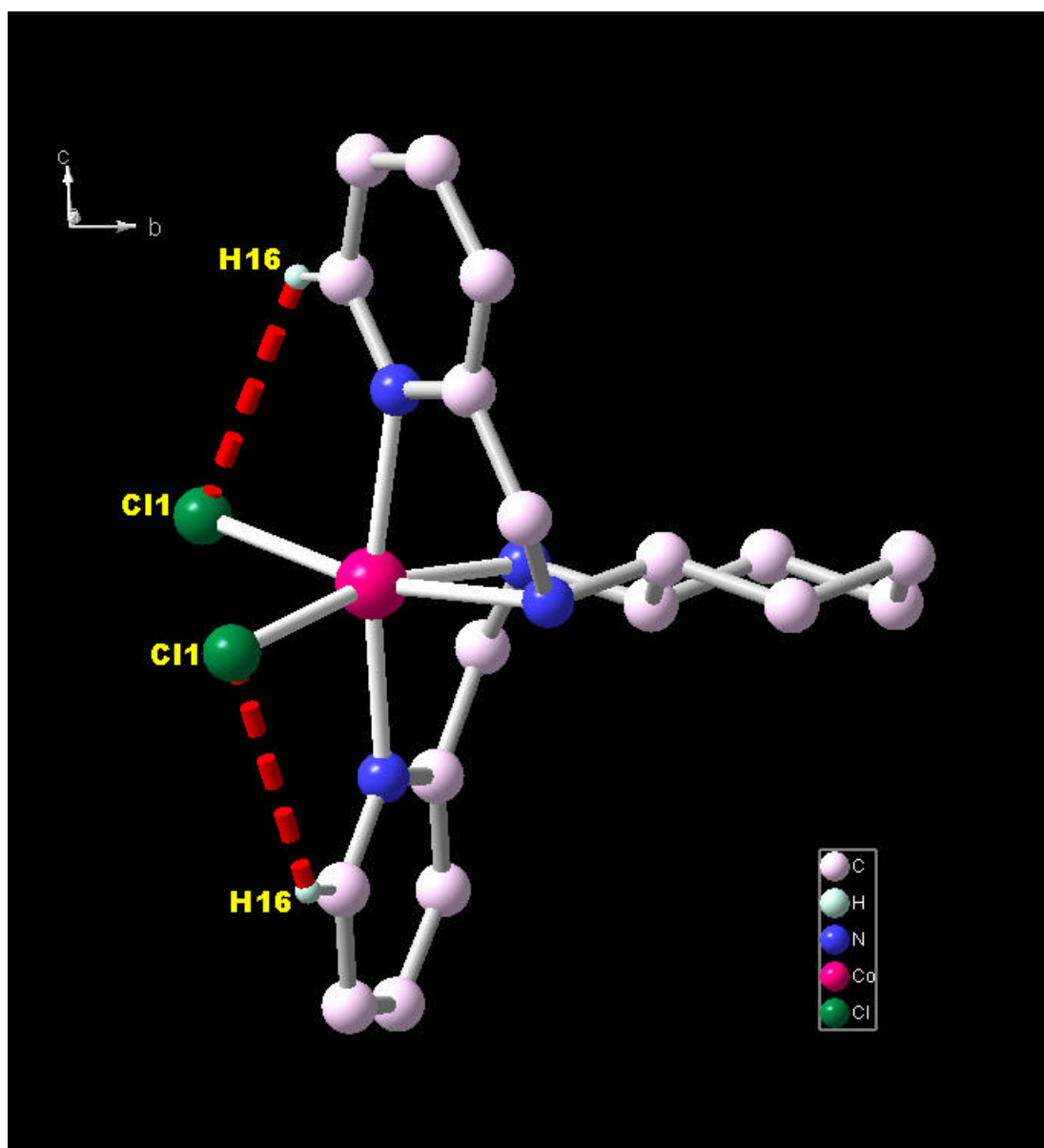


Figure S12

