

SUPPORTING INFORMATION FOR:

Internal hydrogen bonding in tetrahedral and trigonal bipyramidal zinc(II) complexes of pyridine-based ligands

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Figure captions

Fig. S1 Histogram of the H \cdots X (X = centroid of a phenyl ring) distances found for very short N-H \cdots X (X = centroid of a phenyl ring) H-bonds in organic systems.

Fig. S2 Histogram of the H \cdots X (X = centroid of a phenyl ring) distances found for very short N-H \cdots X (X = centroid of a phenyl ring) H-bonds in metal complexes.

Fig. S3 ^1H VT NMR of $[(\text{L}^2)\text{Zn}(\text{Cl})](\text{Cl})$ **2'** in CD_3CN (28 mM) showing aromatic and NH_2 (*) resonances. See Table 7 and compare with Figs. 6, S4-S9.

Fig. S4 ^1H VT NMR of $[(\text{L}^2)\text{Zn}(\text{Cl})](\text{Cl})$ **2'** in CD_3CN (14 mM) showing aromatic and NH_2 (*) resonances. See Table 7 and compare with Figs. 6, S3-S9.

Fig. S5 ^1H VT NMR of $[(\text{L}^2)\text{Zn}(\text{Cl})](\text{Cl})$ **2'** in CD_3CN (7 mM) showing aromatic and NH_2 (*) resonances. See Table 7 and compare with Figs. 6, S3-S9.

Fig. S6 ^1H VT NMR of $[(\text{L}^2)\text{Zn}(\text{Cl})](\text{Cl})$ **2'** in CD_3CN (3.5 mM) showing aromatic and NH_2 (*) resonances. See Table 7 and compare with Figs. 6, S3-S9.

Fig. S7 ^1H VT NMR of $[(\text{L}^2)\text{Zn}(\text{Cl})](\text{BPh}_4)$ **2** in CD_3CN (28 mM) showing aromatic and NH_2 (*) resonances. See Table 7 and compare with Figs. 6, S3-S9.

Fig. S8 ^1H VT NMR of $[(\text{L}^2)\text{Zn}(\text{Cl})](\text{BPh}_4)$ **2** in CD_3CN (7 mM) showing aromatic and NH_2 (*) resonances. See Table 7 and compare with Figs. 6, S3-S9.

Fig. S9 ^1H VT NMR of $[(\text{L}^2)\text{Zn}(\text{Cl})](\text{BPh}_4)$ **2** in CD_3CN (1.8 mM) showing aromatic and NH_2 (*) resonances. See Table 7 and compare with Figs. 6, S3-S8.

Fig. S10 Temperature and concentration dependency of the NH_2 chemical shift in the ^1H NMR spectra of **2'**. See Table 7 and compare with Fig. S11.

Fig. S11 Temperature and concentration dependency of the NH_2 chemical shift in the ^1H NMR spectra of **2**. See Table 7 and compare with Fig S10.

Cambridge Structural Database Search.

Evidence of various types of O-H \cdots C and N-H \cdots C hydrogen bonding in crystalline alkynes, alkenes and aromatics has been reported elsewhere.¹ In this report the generality of only very short N-H \cdots π (phenyl, centroid type) hydrogen bonds was investigated searching the 5.24 (November 2002) version of the Cambridge Structural Database (CSD). Only error-free, non-disordered structures with $R < 0.1$ were accepted. The N-H distance was normalised to 1.01 Å and the H \cdots X (X = centroid of a phenyl ring) distance was specified to lie between 0 and 3 Å and the N-H \cdots X angle to be calculated. A total of 41 structures satisfied our arbitrary criteria of very short N-H \cdots X hydrogen bond, H \cdots X < 2.3 Å (Table S1). These crystal structures were scrutinised and separated into organic (27 structures) and inorganic (14 structures). The focus of this search was on investigating what causes very short external N-H \cdots π (phenyl, centroid type) hydrogen bonding in metal complexes compared to organic compounds. Thus, in organic compounds this structural feature is most commonly found (24 of 27 cases) when a R₃N-H⁺ group is the hydrogen bond donor. By contrast, in metal complexes the majority (8 of 14) of short N-H \cdots π (phenyl, centroid type) hydrogen bonds involved a RNH₂-M fragment as the H-bond donor (M = strongly Lewis acidic metal). See text for interpretation of this CSD search. Histograms for the H \cdots X distances (X = centroid of the phenyl ring) are given below (Figs. S1 and S2).

References:

1. M. A. Viswamitra, R. Radhakrishnam, J. Bandekar and G. R. Desiraju, *J. Am. Chem. Soc.*, 1993, **115**, 4868.

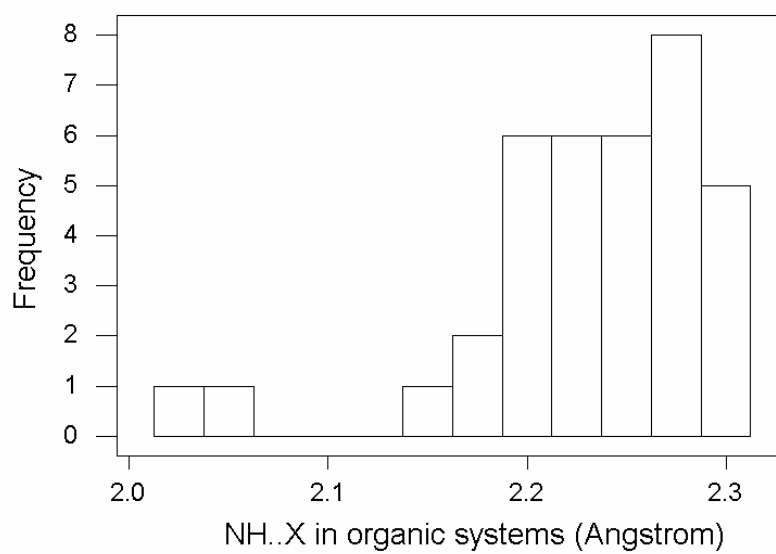


Fig. S1 Mareque Rivas, Salvagni, Torres and Parsons.

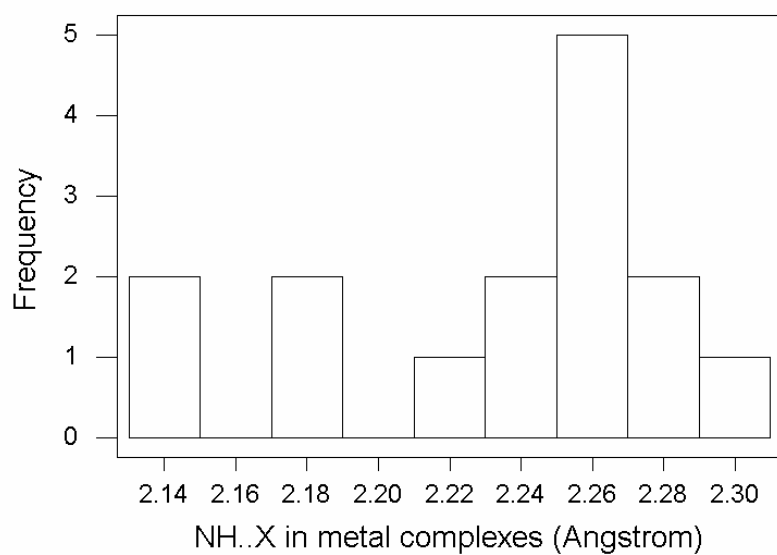


Fig. S2 Mareque Rivas, Salvagni, Torres and Parsons.

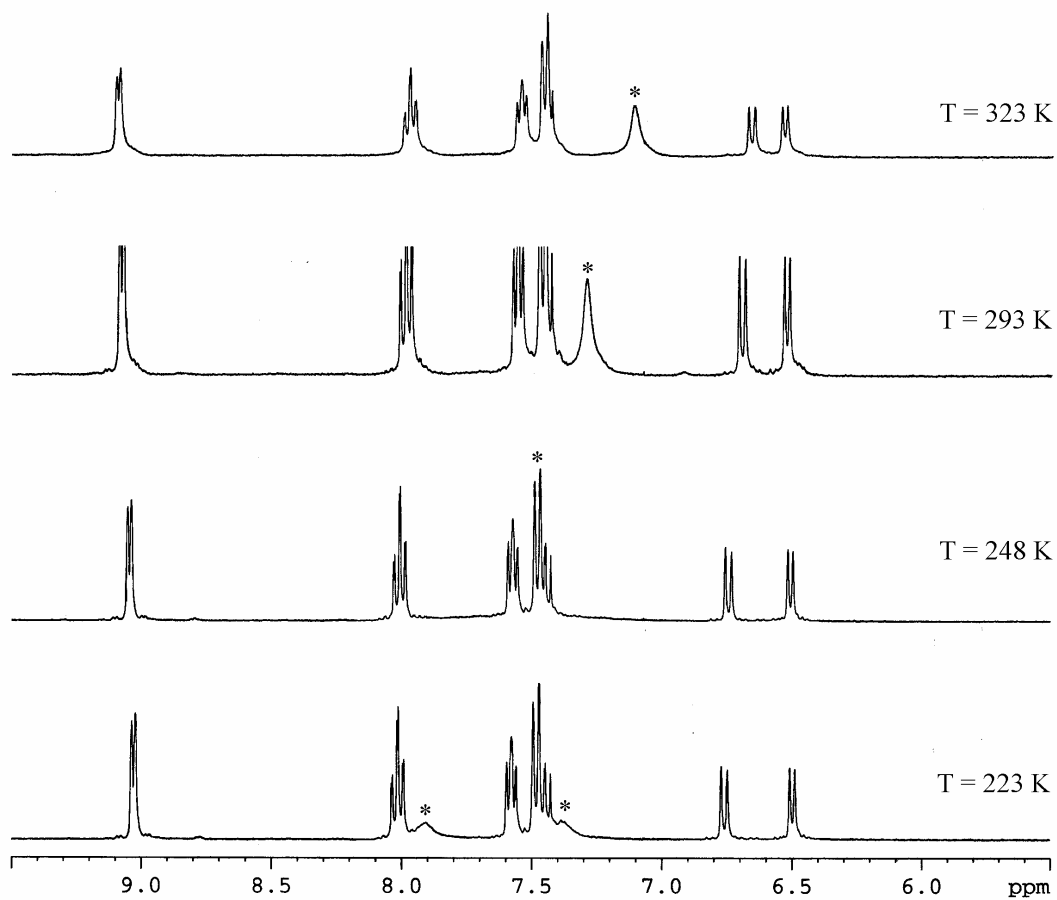


Fig. S3 Mareque Rivas, Salvagni, Torres and Parsons.

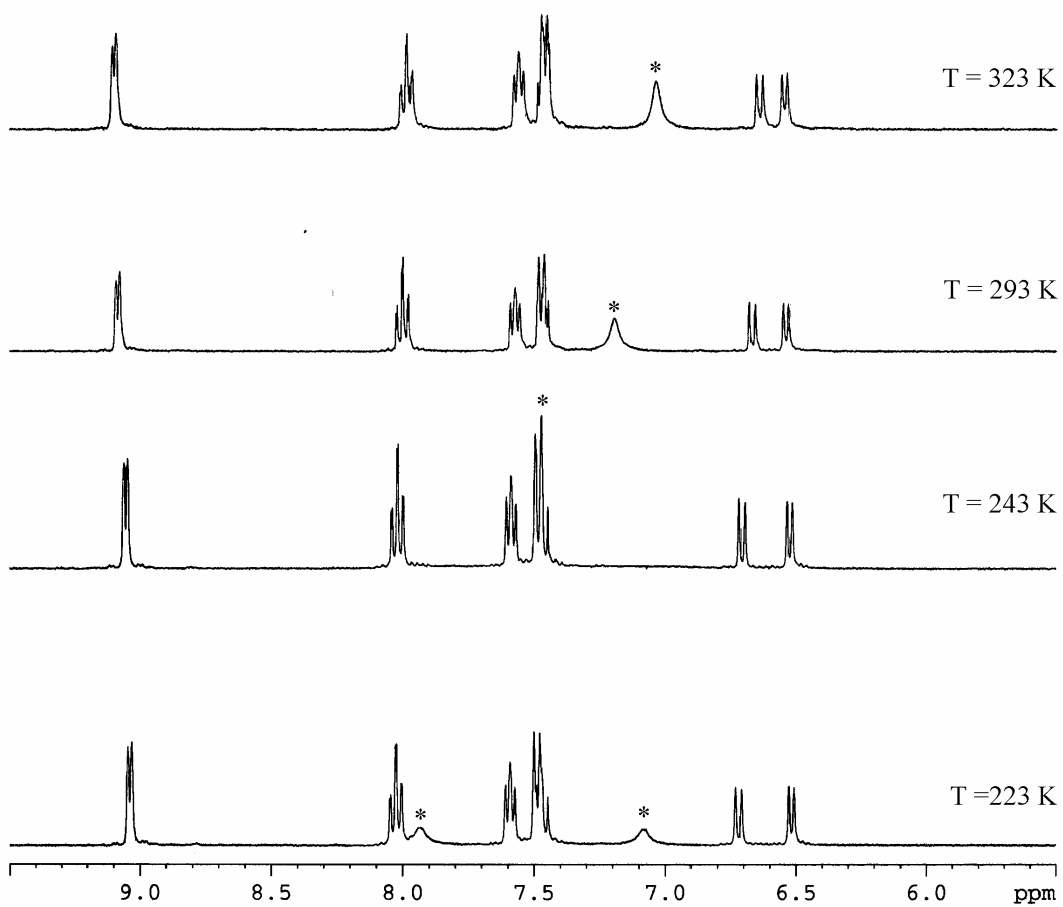


Fig. S4 Mareque Rivas, Salvagni, Torres and Parsons.

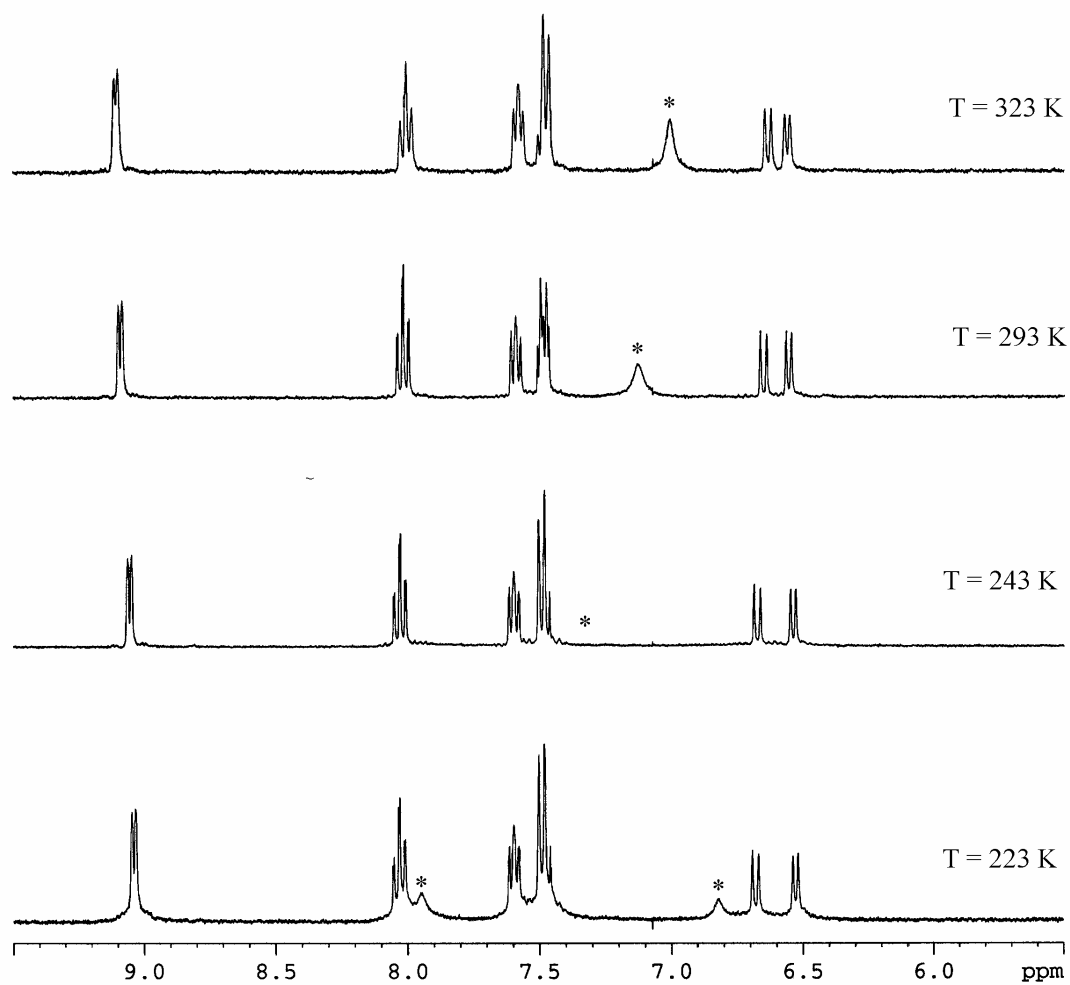


Fig. S5 Mareque Rivas, Salvagni, Torres and Parsons.

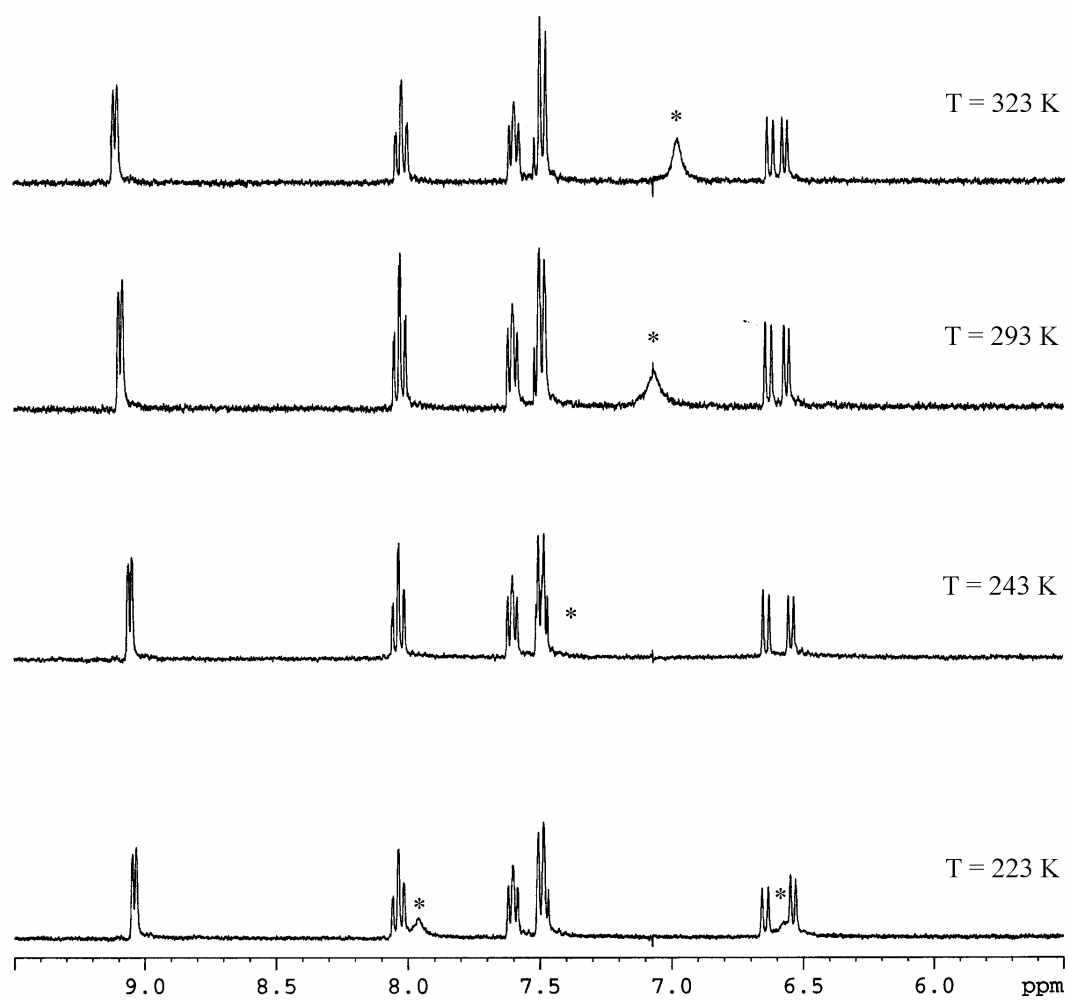


Fig. S6 Mareque Rivas, Salvagni, Torres and Parsons.

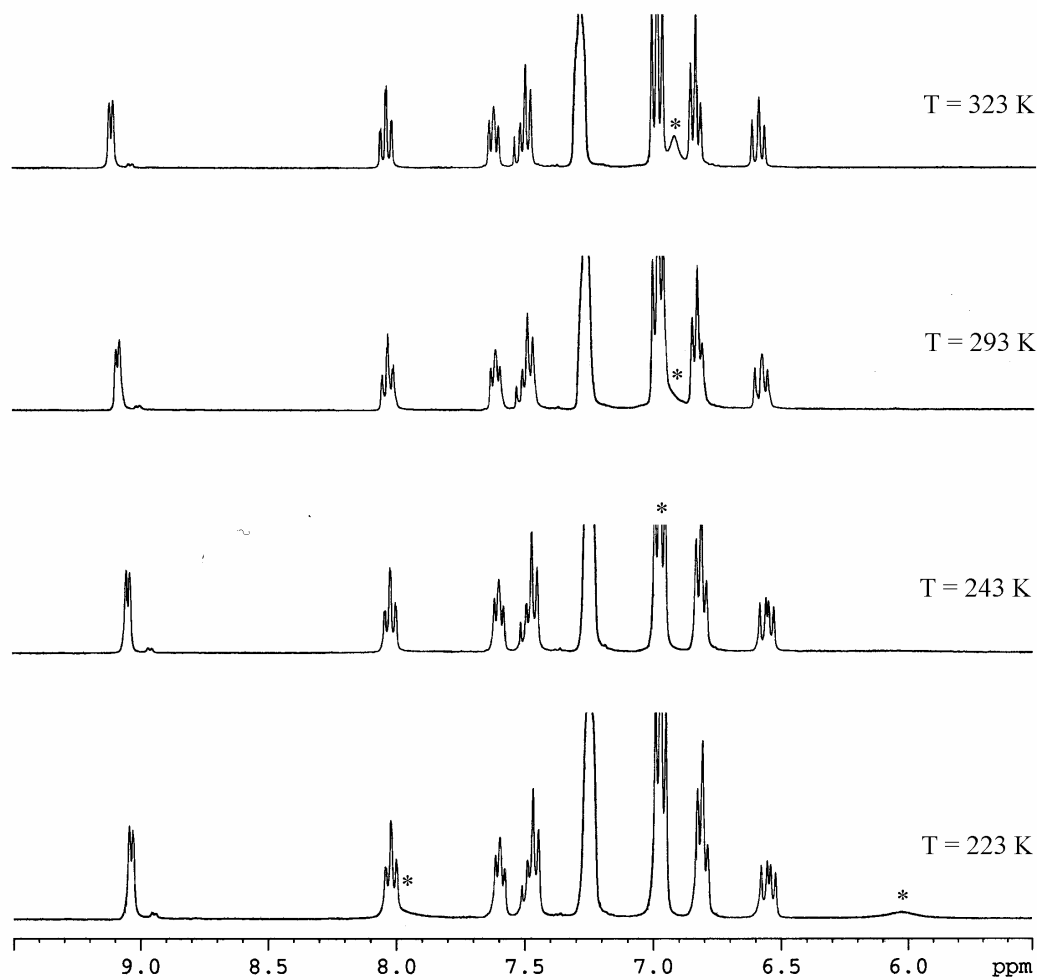


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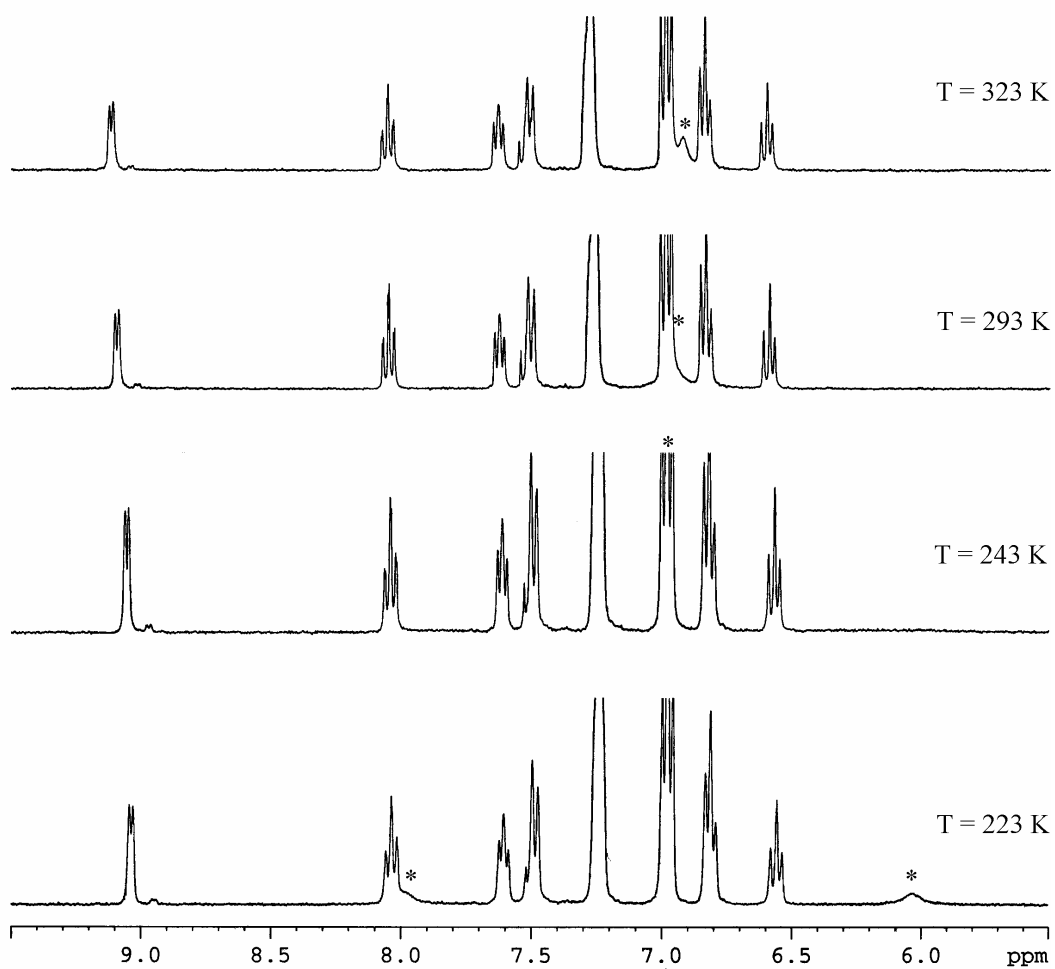


Fig. S8 Mareque Rivas, Salvagni, Torres and Parsons.

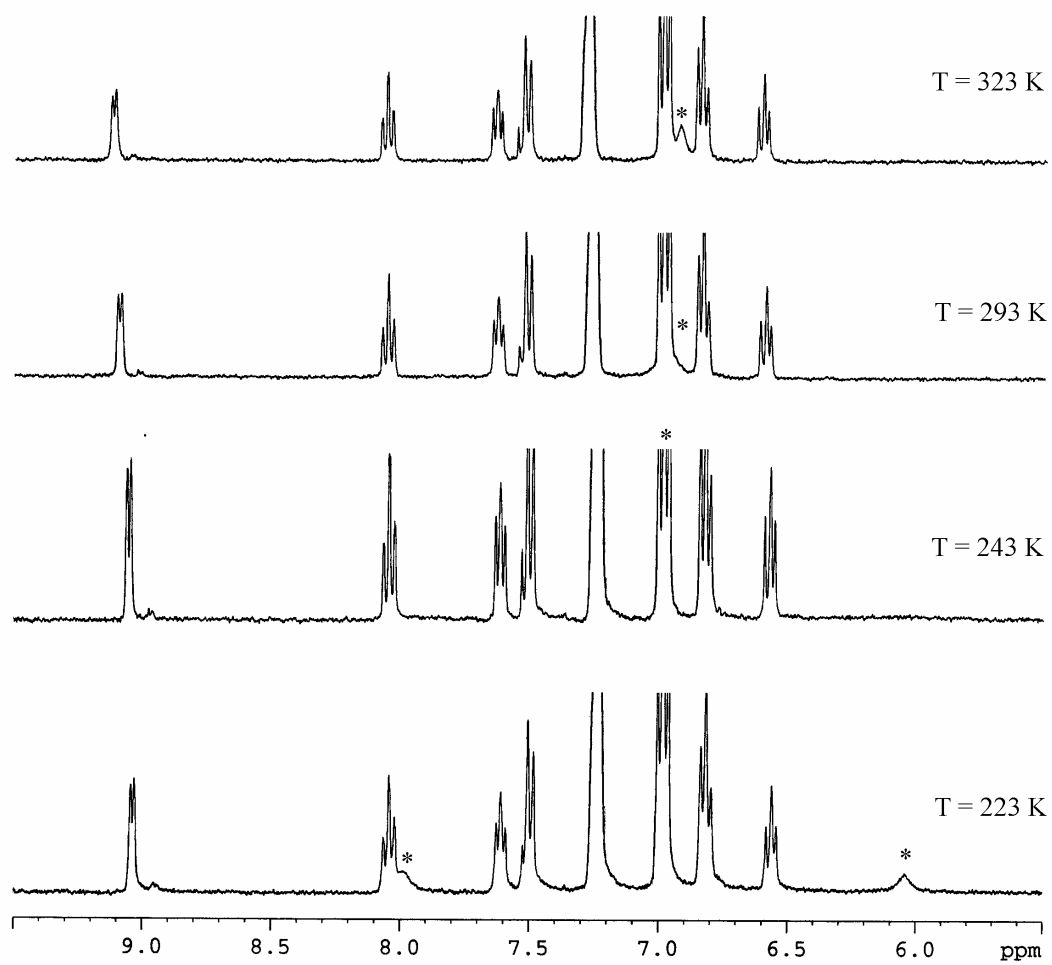


Fig. S9 Mareque Rivas, Salvagni, Torres and Parsons.

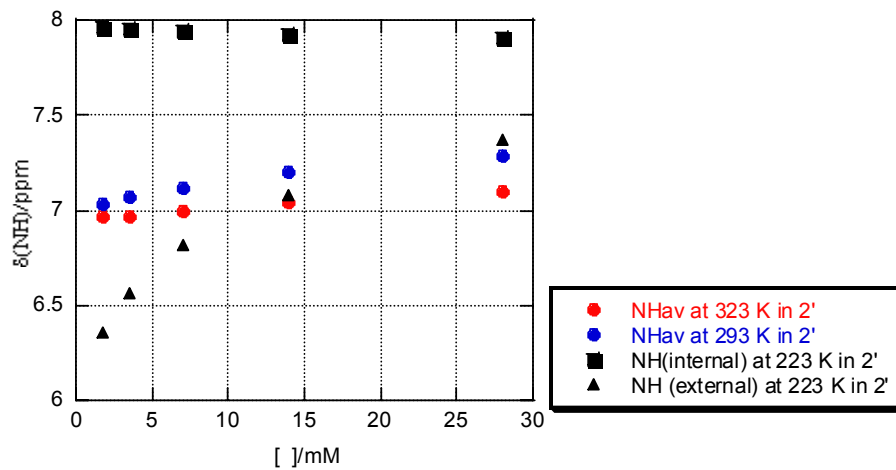


Fig. S10 Mareque Rivas, Salvagni, Torres and Parsons.

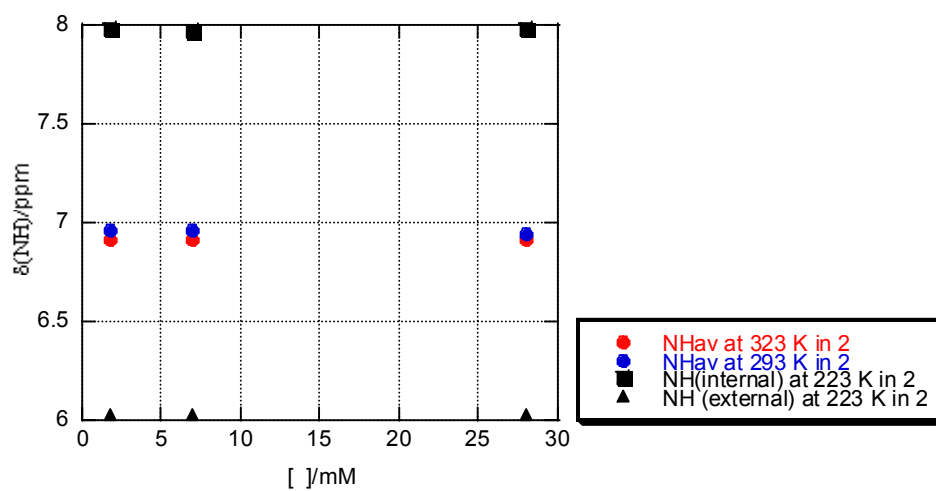


Fig. S11 Mareque Rivas, Salvagni, Torres and Parsons.

Table S1 Refcodes, distances and angles of (i) organic and (ii) inorganic crystal structures with very short N-H...X (X = centroid of a phenyl ring) H-bonds found searching the CSD (5.24 version).

(i)

	N-H...X/°	H...X/Å
ACINUV	165.308	2.233
ACIPOR	169.383	2.237
AMPHEB	141.292	2.181
AMPHEB01	140.994	2.198
AMPHEB02	174.041	2.022
AMPHEB03	171.391	2.046
BUWCAX	153.865	2.251
BUWCAX	154.217	2.273
CAVFOU	166.331	2.292
FIZWOA01	162.169	2.196
GOLDUG	162.694	2.276
GOLDUG	150.285	2.293
HENCIM	157.009	2.295
HENCUY	151.727	2.284
HENDAF	167.954	2.178
HENDIN	170.383	2.212
HENDOT	142.972	2.219
HENDUZ	164.189	2.280
HENFAH	172.703	2.254
HENFAH	149.028	2.251
HENFUB	137.581	2.271
HENGEM	151.859	2.218
HENGEM	158.245	2.142
HENGEM	152.755	2.229
KOVSIK	169.060	2.246
QIJXUC	173.649	2.271
ROHTIR	161.796	2.266
ROHTIR	154.316	2.212
ROHTIR	151.102	2.252
SUVHAS	171.859	2.200
ZOJFOT	166.206	2.197
QEWSEQ	159.518	2.299
SUQLOF	154.141	2.290
SUQLOF	156.504	2.282
SUQLOF	155.414	2.229
SUQLUL	172.268	2.238

(ii)

	N-H...X/°	H...X/Å
DANKEI	169.761	2.266
GEBHIE	160.004	2.173
KOZCAD	148.189	2.286
NEBHUX	137.270	2.296
NOCNEY	163.167	2.184
NOKBAQ	151.258	2.238
RELSOQ	149.619	2.218
REQTEM	167.109	2.230
SIBNAS	146.977	2.281
WODCEX	157.050	2.257
XIHSIQ	161.719	2.262
XIHSIQ	167.235	2.145
YBAENI	169.550	2.264
ZAXBOP	147.054	2.139
ZTANPB	166.595	2.258

