Supplementary Material

Table S1. The dominating role of the Fermi-contact contribution to the indirect nuclear spin-spin coupling constants considered in this work. Values in Hz. The SD term is not available in the deMon-NMR program.

Compound		FC	PSO	DSO	Total
$GeH_3N(PF_2)_2$	^{2}J (P-P)	408.19	-1.98	0.18	406.39
$C_2H_2(PH_2)_2$	^{3}J (P-P)	173.53	-0.06	0.01	173.48
ethane	^{3}J (H-H)	12.68	0.07	-0.10	12.65

Table S2. P…P distances in $GeH_3N(PF_2)_2$ as a function of the P-N-P bond angle.

Angle (deg.)	R(P…P) (Å)
117.0696	2.9019
117.3196	2.9055
117.5696	2.9091
117.8196	2.9128
118.0696	2.9163
118.3196	2.9199
118.5696	2.9234
118.8196	2.9269
119.0696	2.9305
119.3196	2.9341
119.5696	2.9376
119.8196	2.9411
120.0696	2.9446

Table S3. Coefficients in front of the product of the localized molecular orbitals corresponding to the C-H bonds of the interacting protons for different values of the dihedral angle.

Dihedral angle (deg.)	Coefficient (Pipek-Mezey localization)	Coefficient (Boys localization)
0	0.10380	0.10410
15	0.09858	0.09884
30	0.08517	0.08539
45	0.06825	0.06845
60	0.04992	0.05009
75	0.03013	0.03023
90	0.00730	0.00733
105	0.01945	0.01951
120	0.04786	0.04802
135	0.07223	0.07250
150	0.08820	0.08853
165	0.09608	0.09645
180	0.09872	0.09911

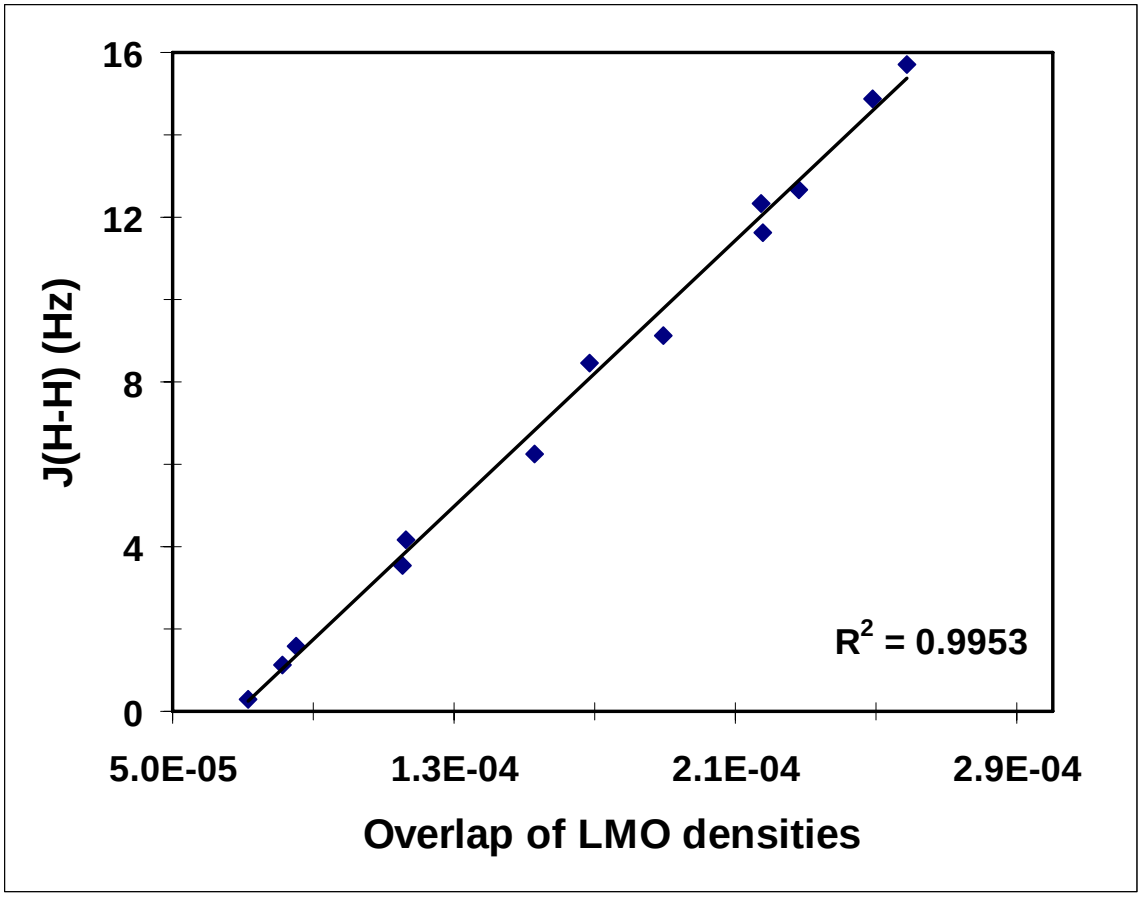

Figure S1. Correlation between $^{3}J^{FC}$(H-H) (Hz) in ethane and the overlap of densities of the unperturbed localized molecular orbitals representing the C-H bonds.