Supporting Information

Fluoride ligands exhibit marked departures from the hydrogen bond acceptor behavior of its heavier halogen congeners

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Table S1. Model geometries (Å, deg) used in ab initio calculations.

Figure S1. Spatially normalized plots[9] of hydrogen bond distances (represented as R_{HX}^3) against angle at the hydrogen (represented as 1 – cos(T), T =180 – (D–H···X)) for hydrogen bonds D–H···X–M; D = C (top), D = N (middle), D = O (bottom), X = F (left), X = Cl, X = Br, X = I (right).

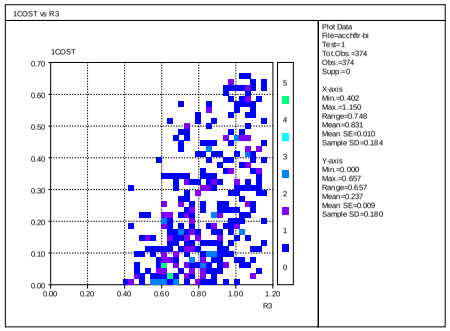
Figure S2. Spatially normalized plots[9] of hydrogen bond distances (represented as R_{HX}^3) against angle at the halogen (represented as 1 – cos(A), A =180 – (H···X–M)) for hydrogen bonds D–H···X–M; D = C (top), D = N (middle), D = O (bottom), X = F (left), X = Cl, X = Br, X = I (right).

Figure S3. Calculated electrostatic potential in the plane perpendicular to the metal coordination plane for the model compounds *trans*-PdX(Me)$(PH_3)_2$; X = F, Cl, Br, I. Electrostatic potential represented with color gradation and contoured at 10 kcal/mol intervals. Only negative and zero contours shown; atoms that lie below the coordination plane are not shown.

Table S1. Model geometries (Å, deg) used in ab initio calculations

Pd-F	1.87 [a]	Pd-P	2.33 [a]
Pd-Cl	2.42 [a]	Pd-C	2.05 [a]
Pd-Br	2.55 [a]	P-H	1.409 [c]
Pd-I	2.75 [a]	C-H	1.095 [c]
P-Pd-X	90.0 [b]	Pd-P-H	118.12 [c]
P-Pd-C	90.0 [b]	Pd-C-H	112.59 [c]
C-Pd-X	180.0 [b]		

a) taken from representative literature crystal structures
b) idealized
c) derived by geometry optimization on the fluoride complex with heavy atom positions fixed.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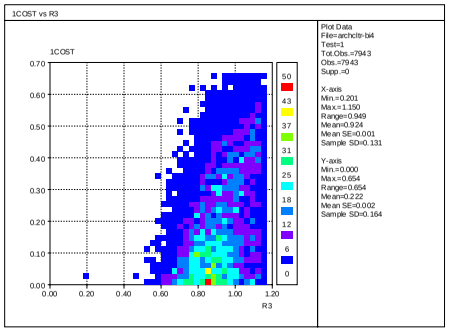
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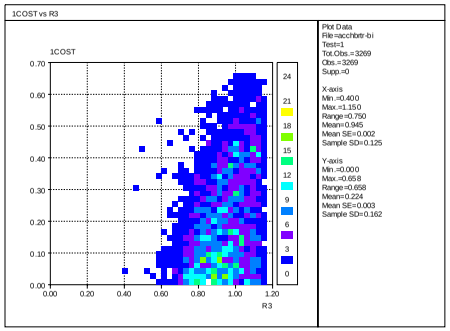
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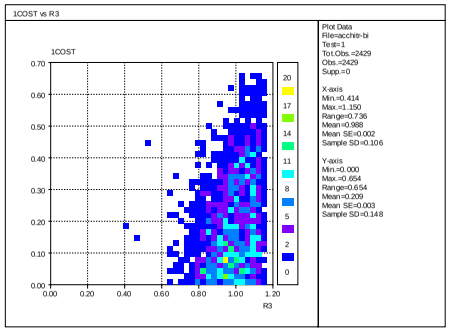
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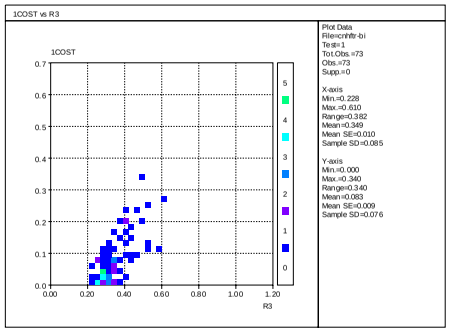
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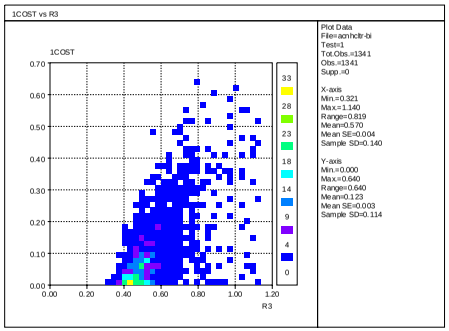
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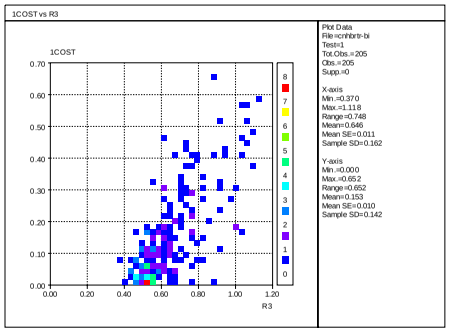
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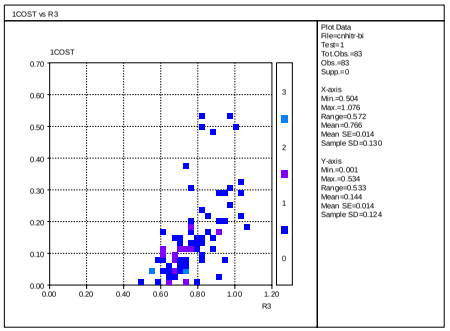
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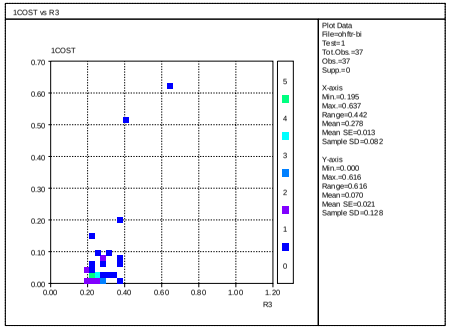
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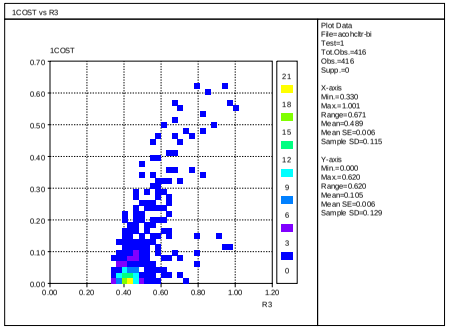
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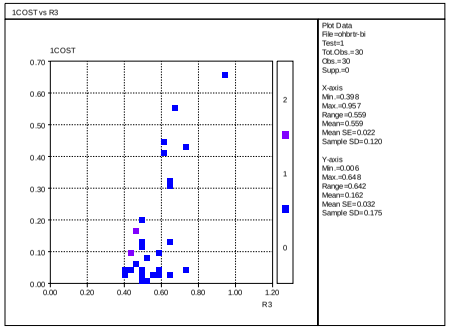
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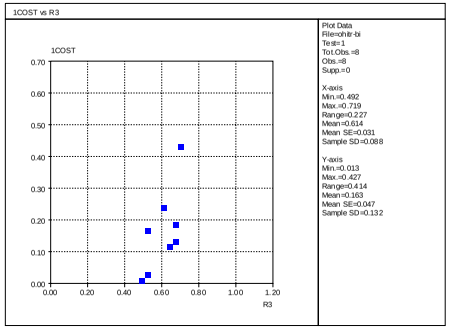
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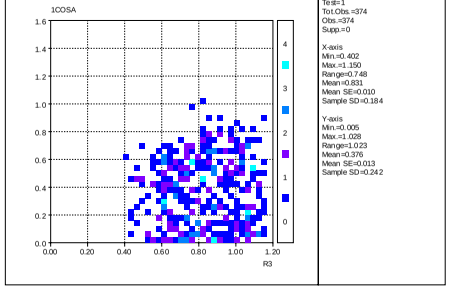

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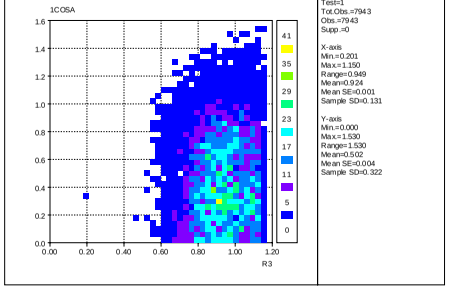

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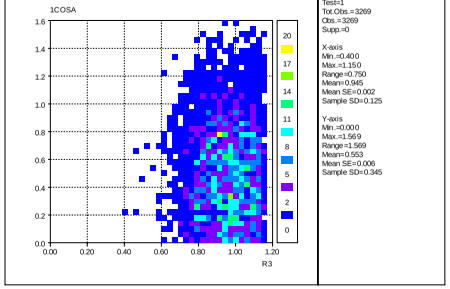

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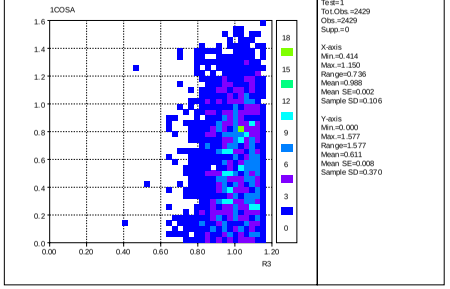

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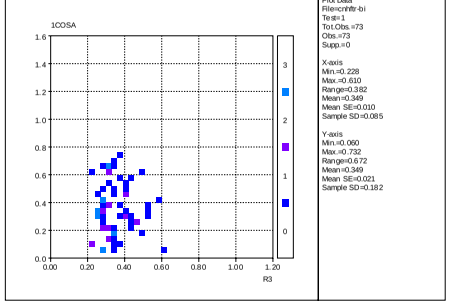

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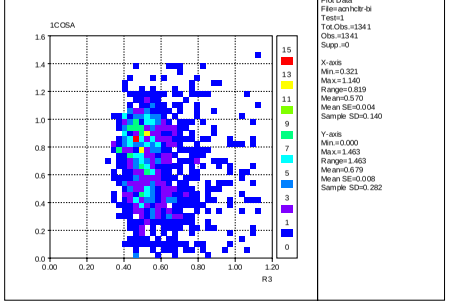

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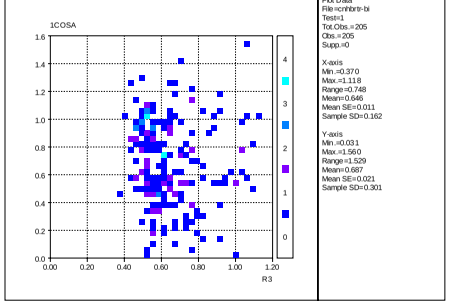

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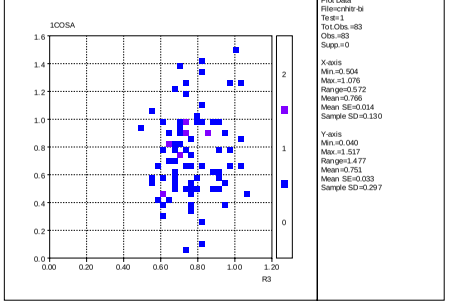

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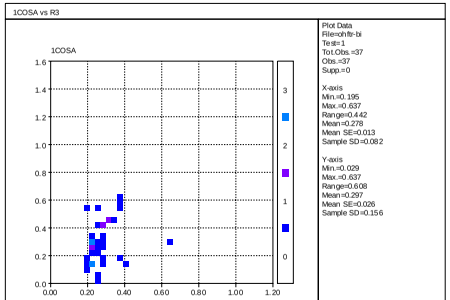

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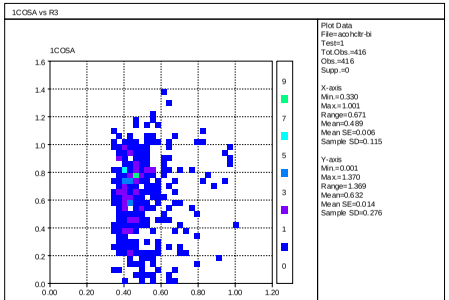

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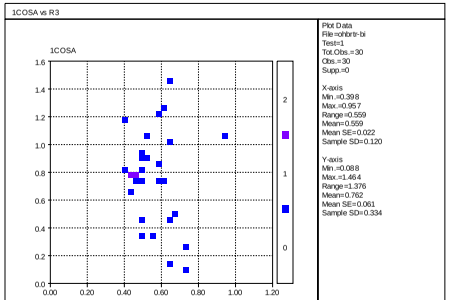

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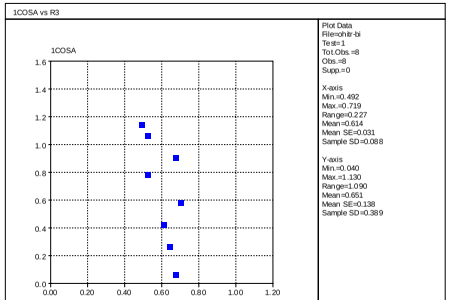

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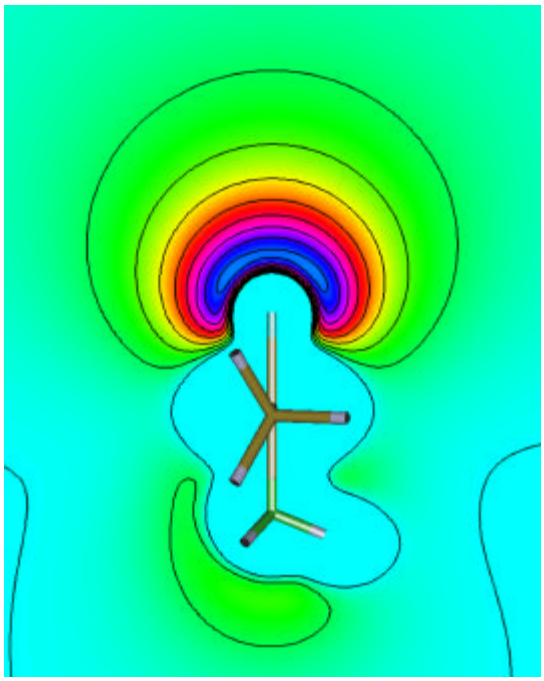

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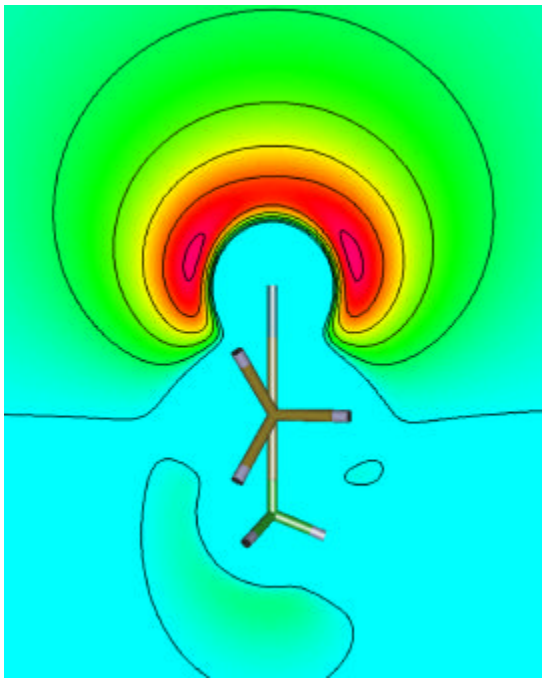

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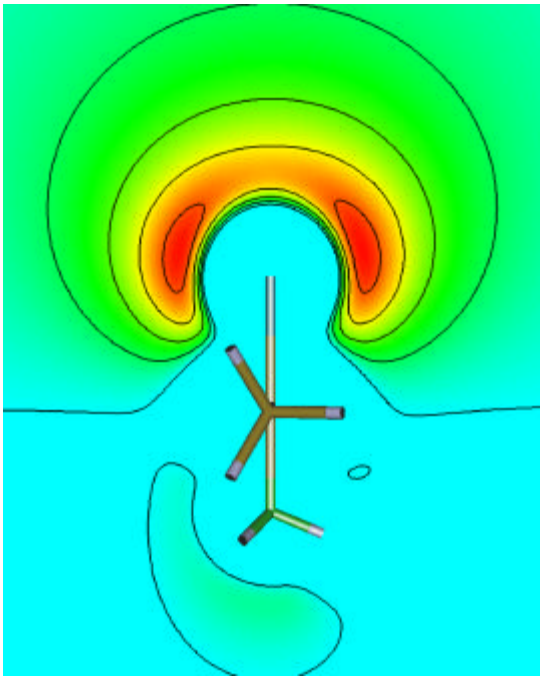

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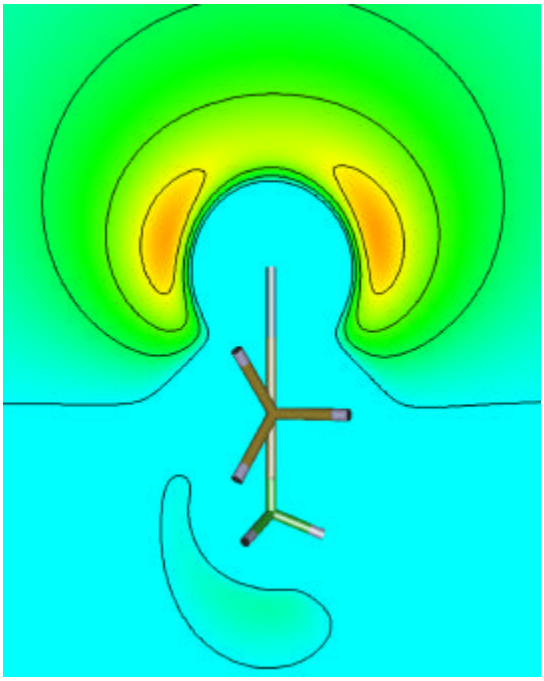

$PdI(Me)(PH_3)_2$

Figure S3.