Supplementary Information

Cyclic phosphazene derivatives combined with two different forms of the phenol-pyrazol group: synthesis, spectroscopic, crystallographic, and stereochemical aspects

Ceylan Mutlu Balcı[*]*, Duygu Palabıyık, Serap Beşli*

Department of Chemistry, Gebze Technical University, Gebze-Kocaeli, Turkey

Materials and Physical Measurements

Hexachlorocyclotriphosphazene, trimer (Sigma-Aldrich, 99%) was purified by fractional crystallization from *n*-hexane (Merck, ≥98%). 2-(1*H*-Pyrazol-3-yl) phenol (Sigma-Aldrich, 97%), dichloromethane, DCM (Merck, ≥99.99), *n*-hexane (Merck, ≥98%), *n*-heptane (Merck, ≥99) were used commercially. Tetrahydrofuran, THF (Sigma-Aldrich, ≥99.9) was distilled over Na-K alloy in an argon atmosphere. Sodium hydride, 60% dispersion in mineral oil (Merck); prior to use, the oil was removed by washing with *n*-hexane followed by decantation. The reaction was performed under an argon atmosphere. $CDCl_3$ (99.8 atom % D) for NMR spectroscopy was also obtained from Merck. Analytical Thin Layer Chromatography (TLC) was performed on Merck silica gel plates (Merck, Kieselgel 60, 0.25 mm thickness) with F_{254} indicator. Column chromatography was performed on silica gel (Merck, Kieselgel 60, 230-400 mesh; for 3 g. crude mixture, 100g. silica gel was used). Elemental analysis data was obtained using an Elementar Vario MICRO Cube. Molecular masses were measured using a Bruker MALDI–TOF (Matrix-Assisted Laser Desorption/Ionization-Time-Of-Flight) spectrometer using 2,5-dihydroxybenzoic acid (Alfa Aesar, 99%) as a matrix for compounds **3**, **6**, **7**, and 1,8,9-trihydroxyanthracene (TCI, >95%) as a matrix for compounds **4a/4b**, **5**, and **8a/8b**. The reaction was performed under an argon atmosphere. ^{31}P NMR spectra were recorded for all compounds in $CDCl_3$ on a Varian INOVA 500 MHz spectrometer using 85% H_3PO_4 as an external reference for ^{31}P NMR measurements. A Bruker DPX 400 MHz spectrometer was used to measure ^{1}H and ^{13}C NMR spectra. FT-IR analysis of **3**, **5**, **6** and **7** were recorded with Perkin Elmer Spectrum 100 spectrophotometer

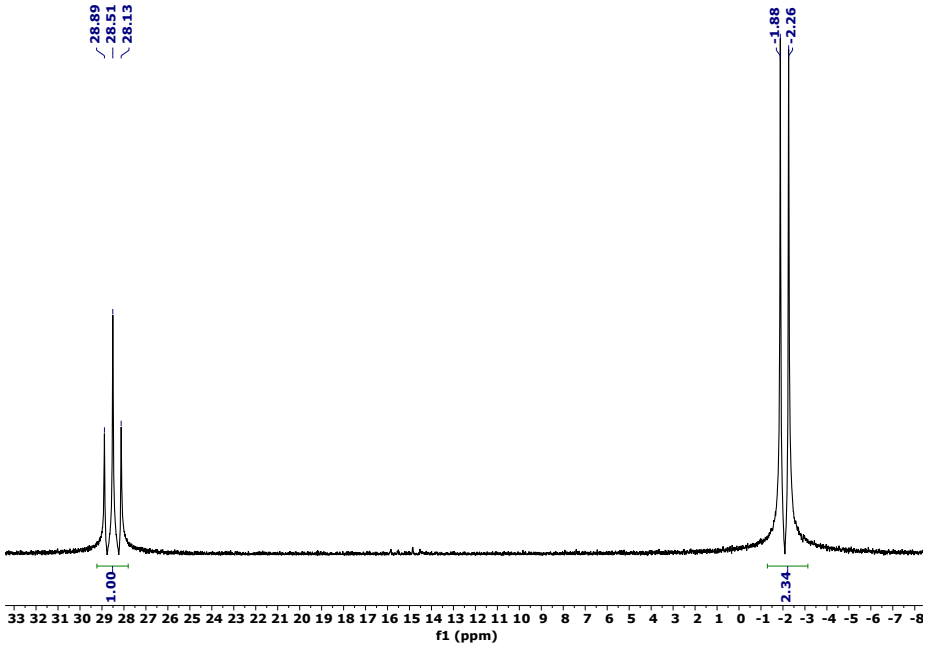

Figure S1. ^{31}P NMR spectrum of compound **5**

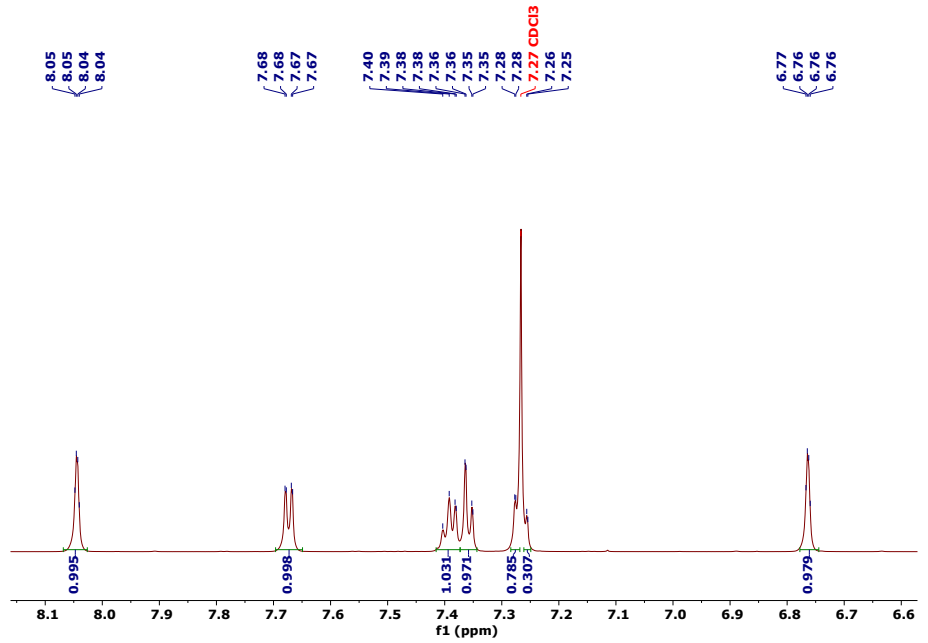

Figure S2. ^{1}H NMR spectrum of compound **5**

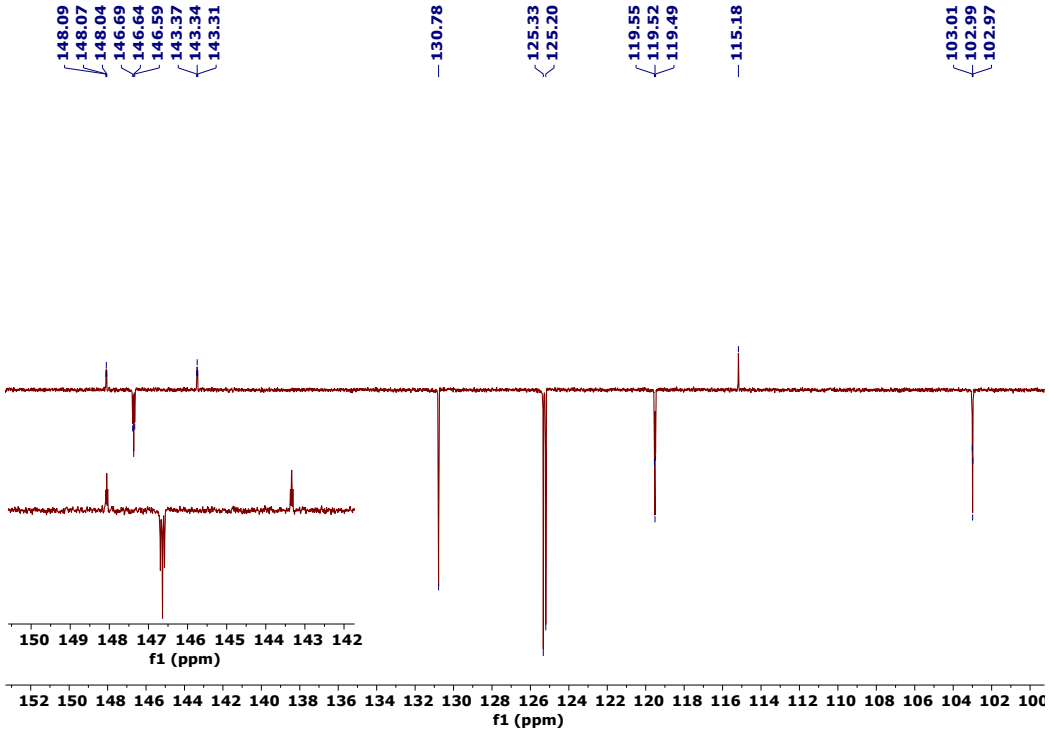

Figure S3. ^{13}C APT NMR spectrum of compound **5**

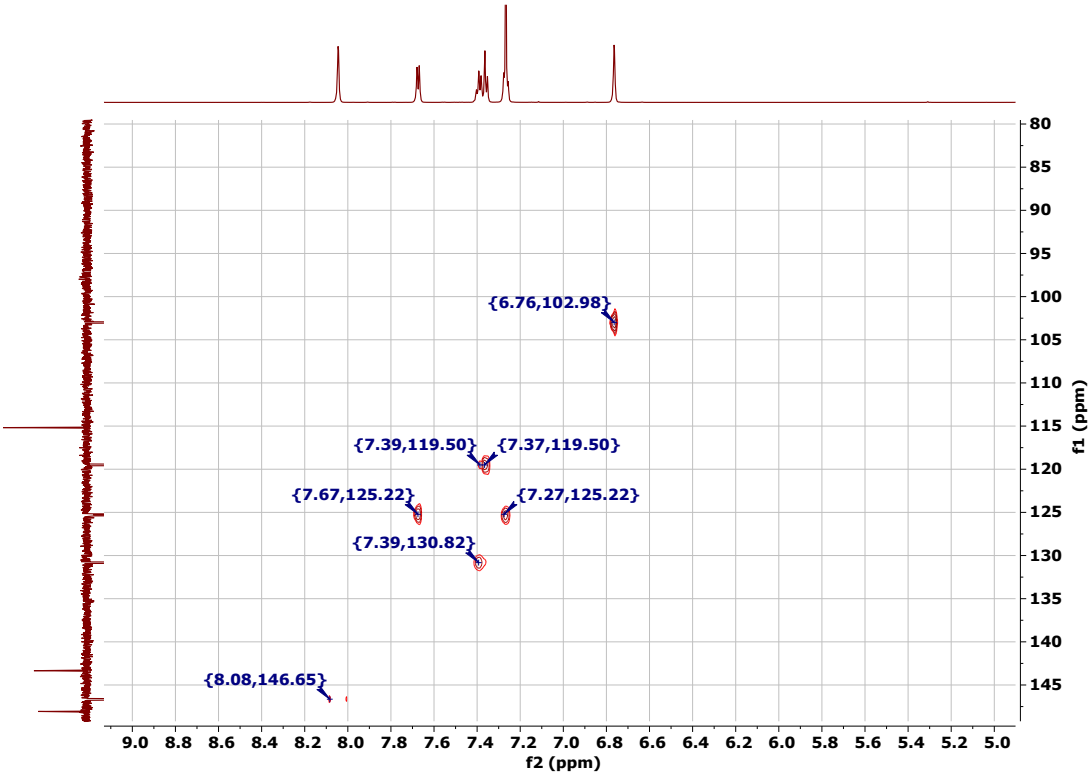

Figure S4. 2D HETCOR NMR spectrum of compound **5**

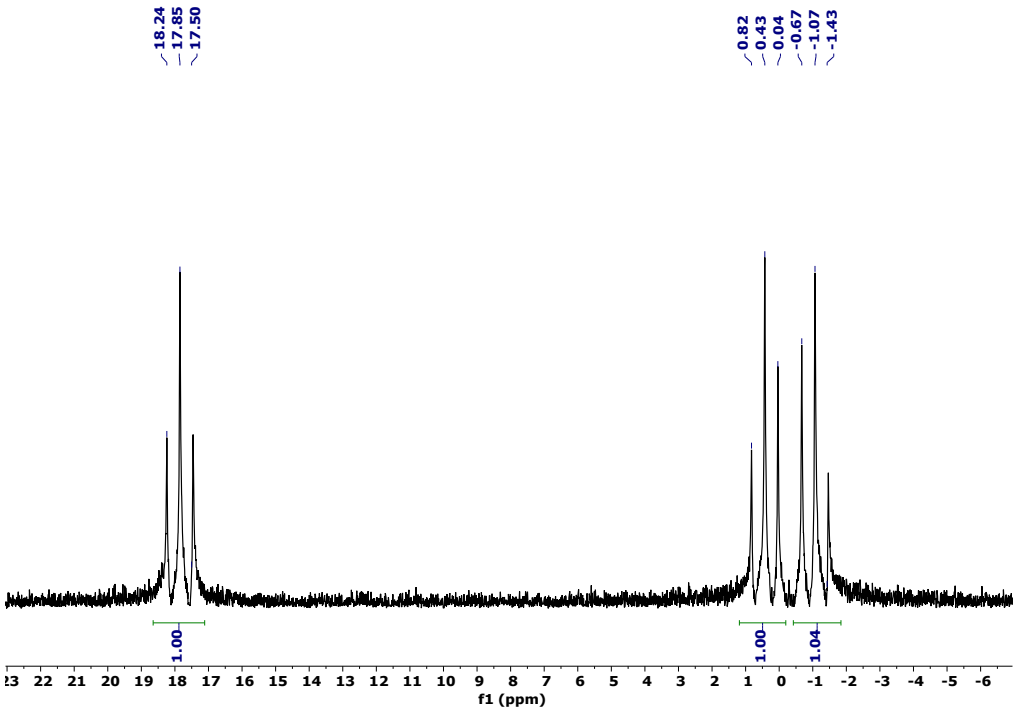

Figure S5. ^{31}P NMR spectrum of compound **6**

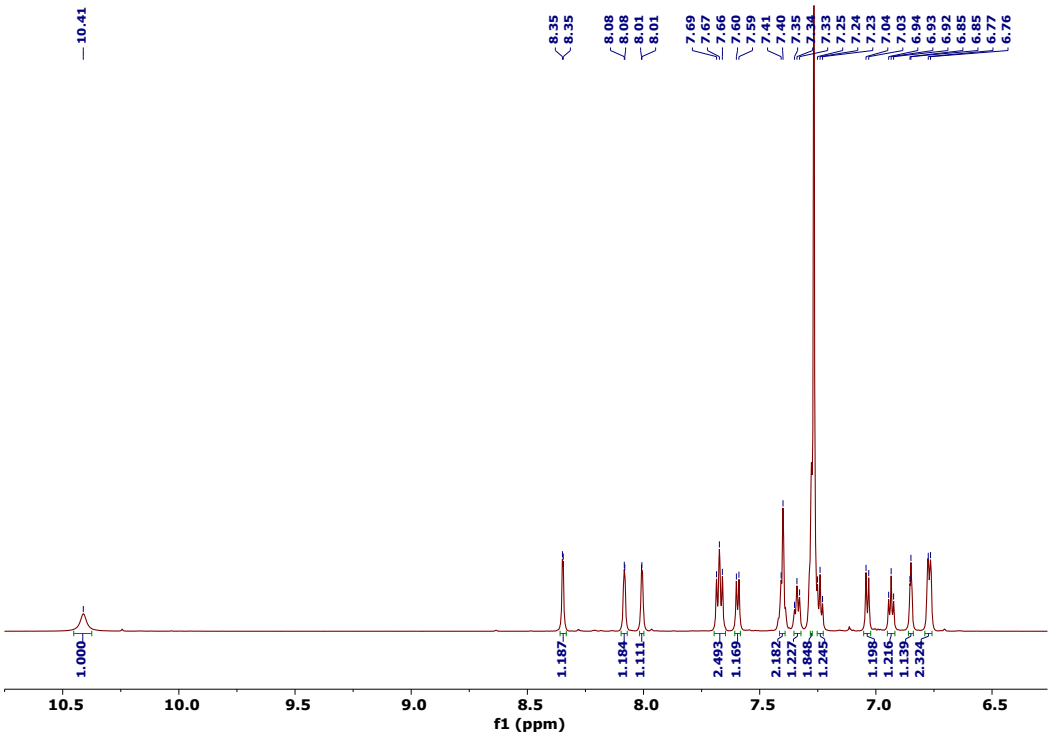

Figure S6. ^{1}H NMR spectrum of compound **6**

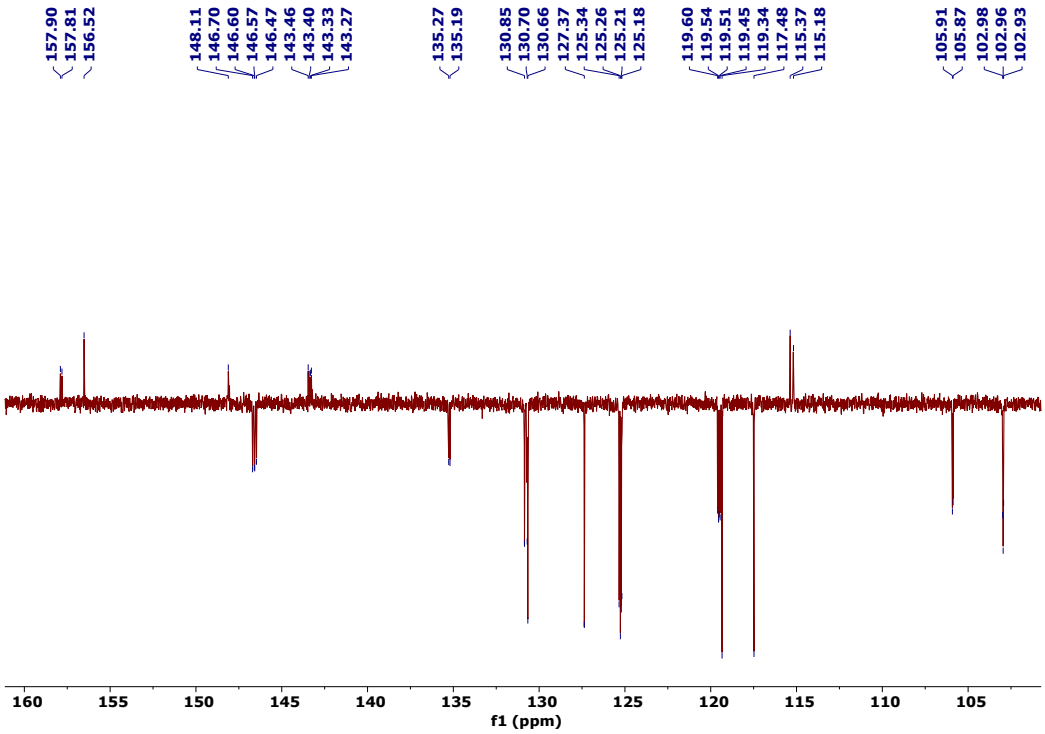

Figure S7. ^{13}C APT NMR spectrum of compound **6**

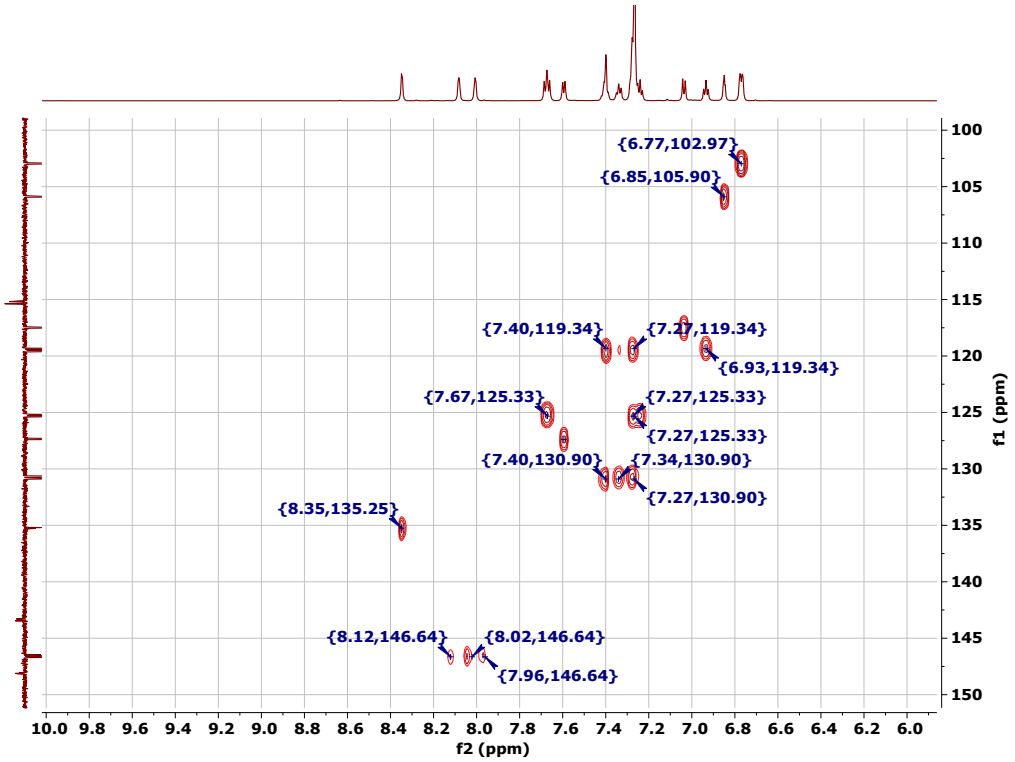

Figure S8. 2D HETCOR NMR spectrum of compound **6**

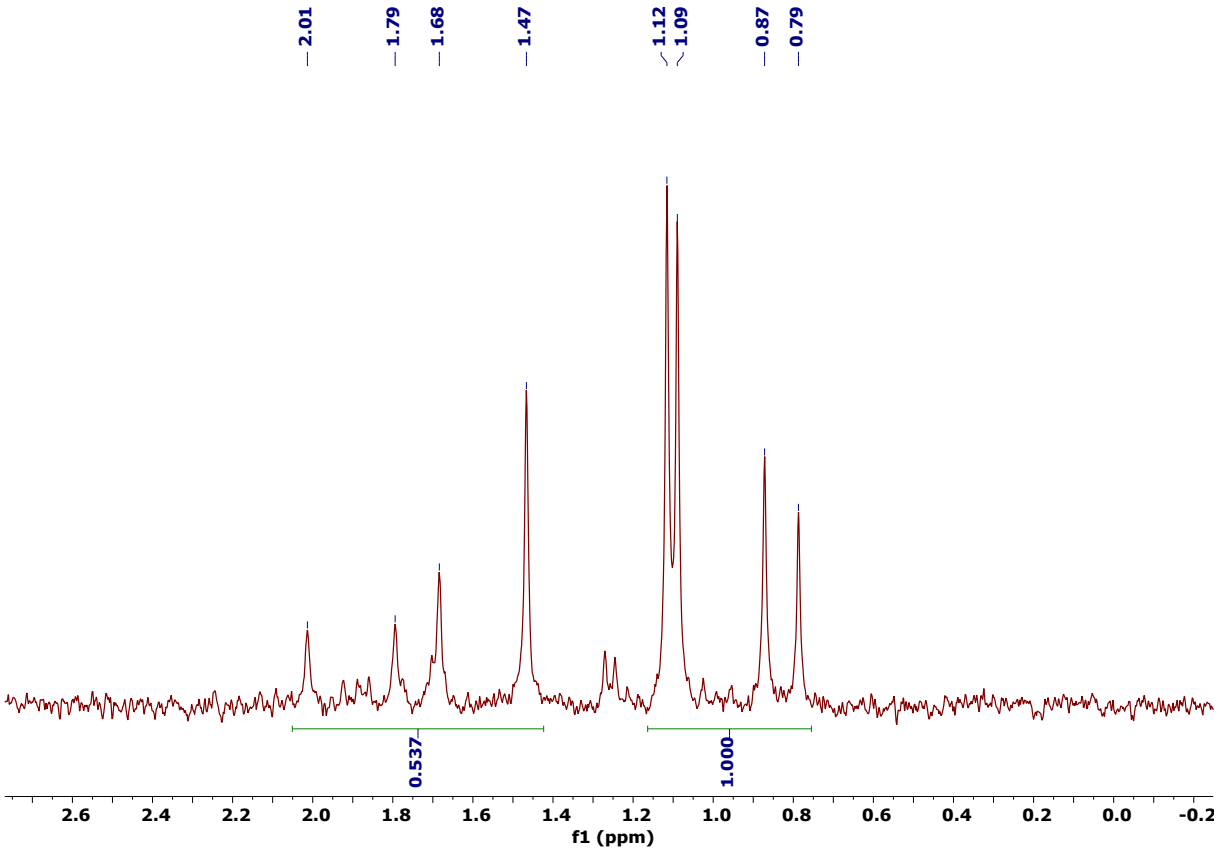

Figure S9. ^{31}P NMR spectrum of compound **7**

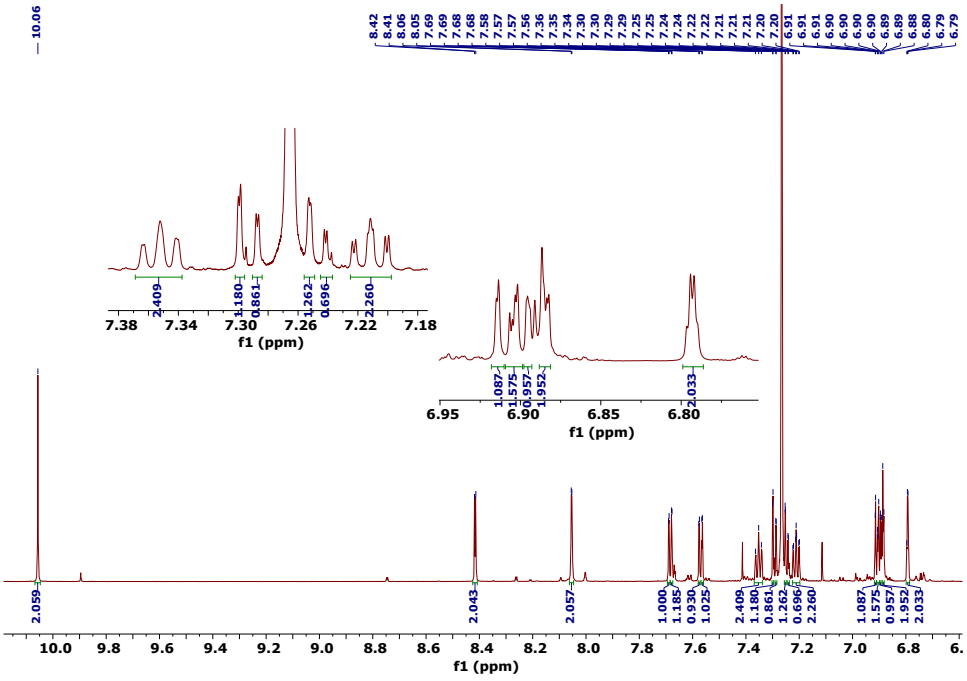

Figure S10. ^{1}H NMR spectrum of compound **7**

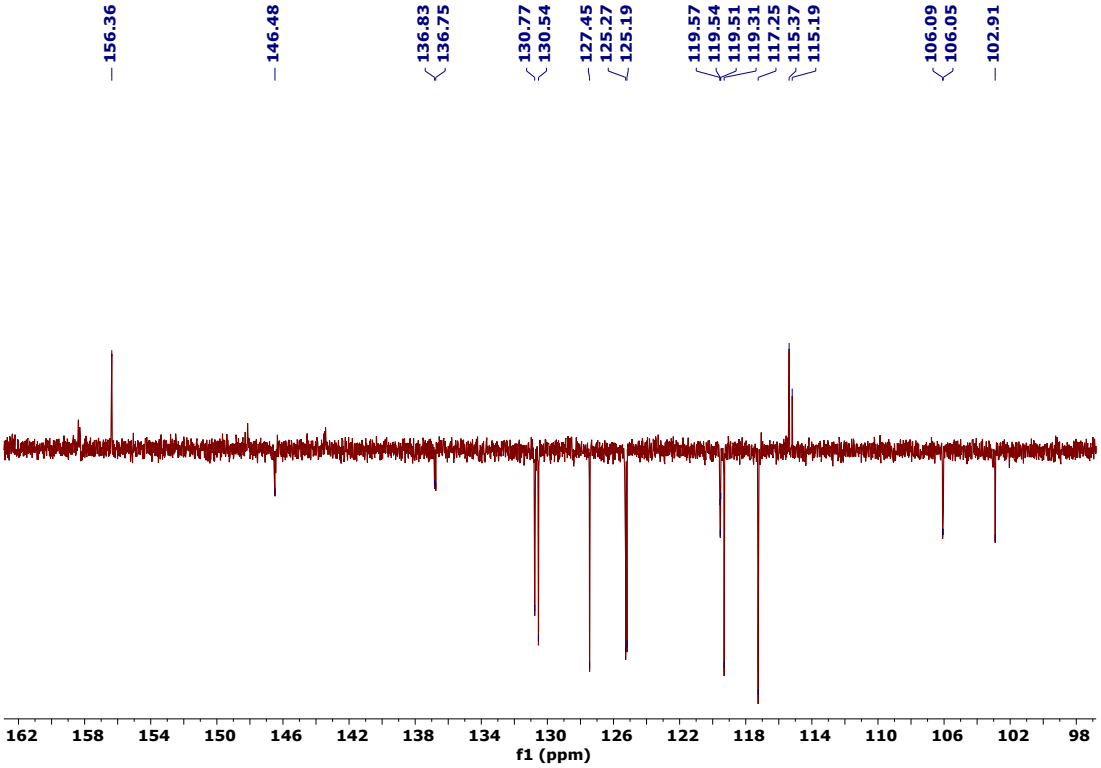

Figure S11. ^{13}C APT NMR spectrum of compound **7**

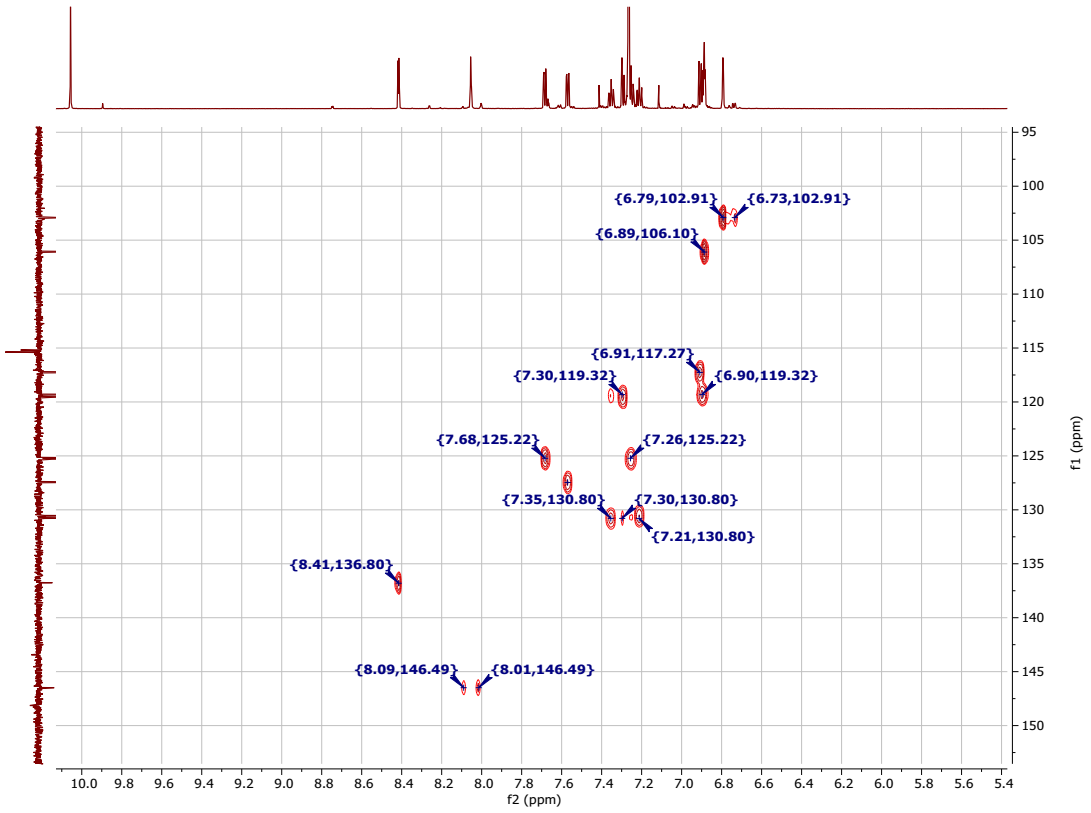

Figure S12. 2D HETCOR NMR spectrum of compound **7**

Table S1. Bond Lengths for compounds **3** and **5**

Compound 3		Compound 5		Compound 5		Compound 5	
Atoms	**Length/Å**	**Atoms**	**Length/Å**	**Atoms**	**Length/Å**	**Atoms**	**Length/Å**
Cl1-P2	1.9869(9)	P1-O1	1.5816(14)	N11- N12	1.378(2)	C22-C27	1.394(3)
Cl2-P2	1.9866(9)	P1-N5	1.6788(16)	N11- C21	1.375(2)	C22-C21	1.453(3)
Cl3-P3	1.9927(10)	P1-N3	1.5878(17)	N13 -N14	1.375(2)	C22-C23	1.396(3)
Cl4-P3	1.9718(9)	P1-N1	1.5769(16)	N13 -C30	1.378(2)	C27-C26	1.376(3)
P1-O1	1.5711(17)	P4-O3	1.5805(14)	N12 -C19	1.324(2)	C21-C20	1.371(3)
P1-N1	1.572(2)	P4-N11	1.6848(15)	N6- C10	1.324(3)	C18-C17	1.381(3)
P1-N3	1.578(2)	P4-N8	1.5879(16)	N4 -C1	1.321(3)	C36-C31	1.394(3)
P1-N4	1.673(2)	P4-N9	1.5796(16)	P5- N13	1.6830(16)	C36-C35	1.381(3)
P2-N1	1.576(2)	P3-Cl2	1.9878(7)	P5- N10	1.5858(17)	C31-C30	1.456(3)
P2-N2	1.574(2)	P3-Cl1	2.0006(7)	P5- N9	1.5774(15)	C31-C32	1.395(2)
P3-N2	1.573(2)	P3-N3	1.5776(16)	P6- Cl4	1.9917(7)	C30-C29	1.363(3)
P3-N3	1.572(2)	P3-N2	1.5802(16)	P6- Cl3	1.9906(7)	C1-C2	1.414(3)
O1-C1	1.386(3)	P2-O2	1.5777(14)	P6- N8	1.5770(16)	C20-C19	1.408(3)
N4-N5	1.376(3)	P2-N7	1.6780(16)	P6- N10	1.5758(16)	C5-C6	1.374(3)
N4-C7	1.374(3)	P2-N2	1.5856(17)	N14-C28	1.324(3)	C8-C7	1.385(3)
N5-C9	1.316(3)	P2-N1	1.5755(16)	C4-C9	1.390(3)	C7-C6	1.392(3)
C1-C2	1.379(3)	O3-C27	1.400(2)	C4-C3	1.453(3)	C35-C34	1.381(3)
C1-C6	1.385(3)	O1-C9	1.402(2)	C4-C5	1.403(2)	C17-C16	1.384(3)
C2-C3	1.378(4)	O2-C18	1.406(2)	C12-C13	1.453(3)	C11-C10	1.400(3)
C3-C4	1.377(4)	O4-C36	1.407(2)	C12-C11	1.365(3)	C32-C33	1.380(3)
C4-C5	1.383(4)	N5-N4	1.378(2)	C9-C8	1.384(3)	C14-C15	1.373(3)
C5-C6	1.389(3)	N5-C3	1.380(2)	C13-C18	1.387(3)	C23-C24	1.375(3)
C6-C7	1.458(3)	N7-N6	1.376(2)	C13-C14	1.403(3)	C26-C25	1.385(3)
C7-C8	1.358(3)	N7-C12	1.376(2)	C3-C2	1.370(3)	C33-C34	1.388(3)
C8-C9	1.400(4)	C15-C16	1.386(3)	C29-C28	1.405(3)	C25-C24	1.388(3)

Compound 6		Compound 6		Compound 7		Compound 7		Compound 7	
Atoms	**Length/Å**	**Atoms**	**Length/Å**	**Atoms**	**Length/Å**	**Atoms**	**Length/Å**	**Atoms**	**Length/Å**
P1-O1	1.5810(18)	C21-C20	1.414(3)	P3-N3	1.577(4)	N6-C10	1.344(7)	C6-C7	1.383(9)
P1-N4	1.6856(19)	C19-C20	1.354(3)	P3-N2	1.574(4)	N7-C13	1.367(7)	C7-C8	1.401(8)
P1- N1	1.5696(19)	C22-C27	1.397(4)	P3-N8	1.669(4)	C19-C20	1.358(7)	C8-C12	1.365(8)
P1-N3	1.580(2)	C22-C23	1.390(3)	P3-N10	1.674(4)	C20-C21	1.404(7)	C10-C11	1.406(9)
P3-Cl1	1.9935(9)	C16-C15	1.452(3)	P1-O1	1.580(4)	C21-C22	1.463(7)	C11-C13	1.375(8)
P3-N8	1.6833(19)	C16-C17	1.365(3)	P1-N3	1.567(4)	C22-C23	1.404(8)	C14-C15	1.350(9)
P3-N2	1.574(2)	C1-C6	1.380(4)	P1-N1	1.578(5)	C22-C27	1.393(8)	C14-C9	1.408(8)
P3-N3	1.579(2)	C1-C2	1.373(4)	P1-N4	1.672(5)	C23-C24	1.383(9)	C15-C16	1.407(10)
P2-O2	1.5804(16)	C7-C6	1.448(4)	P2-O2	1.570(4)	C24-C25	1.376(10)	C16-C17	1.379(9)
P2-N6	1.6805(19)	C7-C8	1.367(3)	P2-N1	1.578(5)	C25-C26	1.369(10)	C17-C18	1.369(8)
P2-N1	1.581(2)	C15-C10	1.385(3)	P2-N2	1.574(4)	C26-C27	1.375(8)	C18-C9	1.378(8)
P2-N2	1.570(2)	C15-C14	1.403(3)	P2-N7	1.658(4)	C28-C29	1.332(8)	P6-N14	1.559(4)
O2-C10	1.408(3)	C6-C5	1.407(4)	O3-C27	1.359(7)	C29-C30	1.413(7)	P6-N13	1.577(4)
O1-C1	1.396(3)	C10-C11	1.379(3)	O4-C36	1.360(6)	C30-C31	1.449(7)	P6-N19	1.678(4)
N8-N9	1.374(3)	C18-C17	1.398(4)	O1-C12	1.403(6)	C31-C32	1.383(8)	P6-N21	1.683(4)
N8-C19	1.368(3)	C27-C26	1.399(4)	O2-C18	1.412(6)	C31-C36	1.392(7)	P4-O5	1.573(3)
N4-N5	1.368(3)	C11-C12	1.392(4)	N8-N9	1.389(5)	C32-C33	1.361(8)	P4-N14	1.577(4)
N4-C7	1.378(3)	C23-C24	1.382(4)	N8-C19	1.367(6)	C33-C34	1.365(9)	P4-N12	1.574(4)
N9-C21	1.330(3)	C8-C9	1.387(4)	N9-C21	1.330(6)	C34-C35	1.379(8)	P4-N15	1.689(4)
N6-N7	1.376(3)	C5-C4	1.377(4)	N10-N11	1.394(6)	C35-C36	1.386(8)	P5-O6	1.573(4)
N6-C16	1.374(3)	C14-C13	1.374(4)	N10-C28	1.380(7)	C1-C2	1.399(8)	P5-N12	1.570(4)
N7-C18	1.319(3)	C12-C13	1.375(5)	N11-C30	1.331(6)	C2-C3	1.370(7)	P5-N13	1.574(4)
O3-C27	1.349(3)	C2-C3	1.378(4)	N4-N5	1.368(6)	C3-C4	1.436(7)	P5-N17	1.663(4)
N5-C9	1.324(3)	C3-C4	1.361(5)	N4-C3	1.399(7)	C4-C5	1.398(7)	O7-C63	1.356(6)
C21-C22	1.466(3)	C24-C25	1.376(5)	N5-C1	1.338(7)	C4-C12	1.389(7)	O8-C72	1.359(6)

C25-C26	1.363(4)			N6-N7	1.394(6)	C5-C6	1.364(9)	O5-C45	1.406(6)

Table S2. Bond Lengths for compounds **6** and **7**

Compound 7		**Compound 7**		**Compound 7**		**Compound 7**		**Compound 7**	
Atoms	**Length/Å**	**Atoms**	**Length/Å**	**Atoms**	**Angle/º**	**Atoms**	**Angle/º**	**Atoms**	**Angle/º**
O6-C54	1.410(6)	C67-C72	1.384(7)	N3-P3-N8	113.1(2)	C21-N9-N8	104.6(4)	O3-C27-C26	116.5(5)
N19-N20	1.379(5)	C68-C69	1.391(8)	N3-P3-N10	105.1(2)	N11-N10-P3	121.2(3)	C26-C27-C22	120.4(6)
N19-C55	1.362(7)	C69-C70	1.368(8)	N2-P3-N3	118.4(2)	C28-N10-P3	127.0(4)	C29-C28-N10	106.5(5)
N20-C57	1.330(6)	C70-C71	1.354(8)	N2-P3-N8	105.1(2)	C28-N10-N11	110.5(4)	C28-C29-C30	108.1(5)
N21-N22	1.380(5)	C71-C72	1.393(7)	N2-P3-N10	111.9(2)	C30-N11-N10	105.1(4)	N11-C30-C29	109.8(5)
N21-C64	1.359(6)	C71-C72	1.393(7)	N8-P3-N10	102.1(2)	N5-N4-P1	120.7(4)	N11-C30-C31	120.3(5)
N22-C66	1.317(6)	C37-C38	1.394(8)	O1-P1-N4	99.0(2)	N5-N4-C3	112.7(4)	C29-C30-C31	129.9(5)
N16-N15	1.375(6)	C38-C39	1.369(7)	N3-P1-O1	107.9(2)	C3-N4-P1	125.4(4)	C32-C31-C30	121.4(5)
N16-C37	1.324(7)	C39-C40	1.441(7)	N3-P1-N1	117.3(2)	C1-N5-N4	103.2(5)	C32-C31-C36	116.5(5)
N15-C39	1.362(6)	C40-C41	1.408(7)	N3-P1-N4	110.0(2)	C10-N6-N7	103.2(5)	C36-C31-C30	122.1(5)
N18-N17	1.380(6)	C40-C45	1.383(7)	N1-P1-O1	110.5(2)	N6-N7-P2	119.3(4)	C33-C32-C31	123.8(6)
N18-C46	1.336(6)	C41-C42	1.368(8)	N1-P1-N4	110.6(2)	C13-N7-P2	128.9(4)	C32-C33-C34	118.4(6)
N17-C48	1.384(6)	C42-C43	1.371(8)	O2-P2-N1	110.4(2)	C13-N7-N6	111.7(4)	C33-C34-C35	120.9(6)
C55-C56	1.345(8)	C43-C44	1.391(8)	O2-P2-N2	108.2(2)	C20-C19-N8	106.4(5)	C34-C35-C36	119.6(6)
C56-C57	1.401(7)	C44-C45	1.374(7)	O2-P2-N7	99.7(2)	C19-C20-C21	106.9(5)	O4-C36-C31	122.9(5)
C57-C58	1.458(7)	C46-C47	1.397(7)	N1-P2-N7	111.1(2)	N9-C21-C20	110.9(5)	O4-C36-C35	116.3(5)
C58-C59	1.390(7)	C47-C48	1.373(7)	N2-P2-N1	117.2(2)	N9-C21-C22	120.4(5)	C35-C36-C31	120.8(5)
C58-C63	1.383(7)	C48-C49	1.440(7)	N2-P2-N7	108.9(2)	C20-C21-C22	128.6(5)	N5-C1-C2	113.0(5)
C59-C60	1.375(8)	C49-C50	1.402(7)	C12-O1-P1	126.3(3)	C23-C22-C21	120.3(5)	C3-C2-C1	106.2(5)
C60-C61	1.378(8)	C49-C54	1.373(7)	C18-O2-P2	126.9(4)	C27-C22-C21	121.4(5)	N4-C3-C4	119.2(5)
C61-C62	1.363(8)	C50-C51	1.386(9)	P1-N3-P3	121.9(3)	C27-C22-C23	118.3(5)	C2-C3-N4	105.0(5)
C62-C63	1.384(7)	C51-C52	1.371(9)	P1-N1-P2	123.0(3)	C24-C23-C22	120.1(7)	C2-C3-C4	135.8(5)

C64-C65	1.359(7)	C52-C53	1.388(8)	P2-N2-P3	121.8(3)	C25-C24-C23	120.4(5)	C5-C4-C3	121.6(5)
C65-C66	1.410(7)	C53-C54	1.369(7)	N9-N8-P3	121.1(3)	C26-C25-C24	119.7(6)	C12-C4-C3	120.7(5)
C66-C67	1.454(6)	C9-C13	1.435(8)	C19-N8-P3	127.4(3)	C25-C26-C27	121.0(7)	C12-C4-C5	117.7(5)
C67-C68	1.384(7)			C19-N8-N9	111.2(4)	O3-C27-C22	123.1(5)	C6-C5-C4	120.4(6)

Table S3. Bond Lengths and bond angles of compound **7**

Compound 7		**Compound 7**		**Compound 7**		**Compound 7**		**Compound 7**	
Atoms	**Angle/º**	**Atoms**	**Angle/º**	**Atoms**	**Angle/º**	**Atoms**	**Angle/º**	**Atoms**	**Angle/º**
C5-C6-C7	121.2(6)	N12-P4-N15	110.6(2)	N18-N17-C48	122.2(4)	C70-C69-C68	119.3(5)	C54-C49-C48	120.8(4)
C6-C7-C8	119.4(6)	O6-P5-N13	108.20(19)	C48-N17-P5	127.9(4)	C71-C70-C69	119.8(5)	C54-C49-C50	117.7(5)
C12-C8-C7	118.6(6)	O6-P5-N17	99.37(19)	C56-C55-N19	106.8(5)	C70-C71-C72	121.1(6)	C51-C50-C49	120.0(6)
C4-C12-O1	120.8(5)	N12-P5-O6	110.5(2)	C55-C56-C57	107.5(5)	O8-C72-C67	122.4(5)	C52-C51-C50	120.4(6)
C8-C12-O1	116.4(5)	N12-P5-N13	116.8(2)	N20-C57-C56	109.5(5)	O8-C72-C71	117.1(5)	C51-C52-C53	120.3(6)
C8-C12-C4	122.8(5)	N12-P5-N17	111.5(2)	N20-C57-C58	120.3(4)	C67-C72-C71	120.5(5)	C54-C53-C52	118.5(6)
N6-C10-C11	112.7(6)	N13-P5-N17	109.0(2)	C56-C57-C58	130.3(5)	N16-C37-C38	113.3(5)	C49-C54-O6	120.7(5)
C13-C11-C10	105.1(5)	C45-O5-P4	126.3(3)	C59-C58-C57	120.0(5)	C39-C38-C37	104.7(5)	C53-C54-O6	116.1(5)
C15-C14-C9	119.1(7)	C54-O6-P5	127.9(3)	C63-C58-C57	122.1(5)	N15-C39-C38	106.7(5)	C53-C54-C49	123.1(5)
C14-C15-C16	121.8(6)	P6-N14-P4	121.7(3)	C63-C58-C59	117.9(5)	N15-C39-C40	119.0(5)	C14-C9-C13	121.2(6)
C17-C16-C15	119.2(7)	P5-N12-P4	123.8(2)	C60-C59-C58	121.4(6)	C38-C39-C40	134.3(5)	C18-C9-C14	118.4(6)
C18-C17-C16	118.6(7)	P5-N13-P6	121.1(2)	C59-C60-C61	119.8(6)	C41-C40-C39	121.6(5)	C18-C9-C13	120.4(5)
C17-C18-O2	115.5(5)	N20-N19-P6	121.3(3)	C62-C61-C60	119.5(5)	C45-C40-C41	117.4(5)	N7-C13-C11	107.2(5)
C17-C18-C9	122.8(6)	C55-N19-P6	128.0(4)	C61-C62-C63	121.0(6)	C42-C41-C40	119.6(5)	N7-C13-C9	118.8(5)
C9-C18-O2	121.7(5)	C55-N19-N20	110.3(4)	O7-C63-C58	122.6(5)	C41-C42-C43	121.2(5)	C11-C13-C9	134.0(5)
N14-P6-N13	119.1(2)	C57-N20-N19	105.9(4)	O7-C63-C62	117.1(5)	C42-C43-C44	121.2(5)		
N14-P6-N19	112.8(2)	N22-N21-P6	121.4(3)	C58-C63-C62	120.3(5)	C45-C44-C43	116.7(5)		
N14-P6-N21	104.9(2)	C64-N21-P6	127.6(3)	N21-C64-C65	106.9(5)	C40-C45-O5	120.4(4)		
N13-P6-N19	105.5(2)	C64-N21-N22	110.9(4)	C64-C65-C66	106.1(4)	C44-C45-O5	115.7(5)		

N13-P6-N21	112.4(2)	C66-N22-N21	105.4(4)	N22-C66-C65	110.8(4)	C44-C45-C40	123.9(5)		
N19-P6-N21	100.75(19)	C37-N16-N15	103.2(4)	N22-C66-C67	120.7(4)	N18-C46-C47	112.2(5)		
O5-P4-N14	109.4(2)	N16-N15-P4	121.0(3)	C65-C66-C67	128.5(4)	C48-C47-C46	106.5(5)		
O5-P4-N12	110.5(2)	C39-N15-P4	126.9(3)	C68-C67-C66	120.7(5)	N17-C48-C49	119.0(4)		
O5-P4-N15	99.1(2)	C39-N15-N16	112.0(4)	C68-C67-C72	117.1(5)	C47-C48-N17	105.3(5)		
N14-P4-N15	109.8(2)	C46-N18-N17	103.7(4)	C72-C67-C66	122.2(4)	C47-C48-C49	135.6(5)		
N12-P4-N14	116.1(2)	N18-N17-P5	119.9(3)	C67-C68-C69	122.1(6)	C50-C49-C48	121.5(5)		

Table S4. Bond angles of compound **7**

Compound 3		**Compound 3**		**Compound 5**		**Compound 5**		**Compound 5**	
Atoms	**Angle/º**	**Atoms**	**Angle/º**	**Atoms**	**Angle/º**	**Atoms**	**Angle/º**	**Atoms**	**Angle/º**
O1-P1-N1	109.11(11)	C2-C1-O1	116.3(2)	N10-P6-Cl4	108.21(7)	N1- P2- O2	107.56(8)	C28-N14-N13	102.94(16)
O1-P1-N3	109.42(11)	C2-C1-C6	122.4(2)	N10-P6-Cl3	109.36(7)	N1-P2-N7	111.31(8)	C9-C4-C3	120.45(16)
O1-P1-N4	100.28(9)	C6-C1-O1	121.4(2)	N10-P6-N8	118.37(9)	N1-P2-N2	117.49(8)	C9-C4-C5	117.50(17)
N1-P1-N3	116.51(10)	C3-C2-C1	118.6(2)	O1-P1-N5	99.55(7)	C27-O3-P4	124.30(12)	C5-C4-C3	122.05(17)
N1-P1-N4	110.34(11)	C4-C3-C2	120.3(2)	O1-P1-N3	110.73(9)	C9-O1-P1	125.46(12)	N7-C12-C13	119.49(16)
N3-P1-N4	109.95(11)	C3-C4-C5	120.6 (2)	N3-P1-N5	108.89(8)	C18-O2-P2	126.55(12)	C11-C12-N7	106.29(16)
Cl2-P2-Cl1	101.50(4)	C4-C5-C6	120.1(2)	N1-P1-O1	107.83(8)	C36O4-P5	123.76(12)	C11-C12-C13	134.17(17)
N1-P2-Cl1	108.75(9)	C1-C6-C5	118.0(2)	N1-P1-N5	110.74(9)	N4-N5-P1	121.52(12)	C4-C9-O1	120.47(16)
N1-P2-Cl2	109.40(9)	C1-C6-C7	120.07(19)	N1-P1-N3	117.61(8)	N4-N5-C3	112.00(15)	C8-C9-O1	116.71(17)
N2-P2-Cl1	108.95(9)	C5-C6-C7	121.9(2)	O3-P4-N11	99.06(7)	C3-N5-P1	123.99(13)	C8-C9-C4	122.79(17)
N2-P2-Cl2	108.31(9)	N4-C7-C6	119.71(19)	O3-P4-N8	111.01(8)	N6-N7-P2	120.47(12)	C18-C13-C12	120.31(16)
N2-P2-N1	118.58(10)	C8-C7-N4	106.4(2)	N8-P4-N11	107.84(8)	C12-N7-P2	127.01(13)	C18-C13-C14	117.51(17)
Cl4-P3-Cl3	101.26(5)	C8-C7-C6	133.9(2)	N9-P4-O3	107.51(8)	C12-N7-N6	112.05(15)	C14-C13-C12	122.15(18)
N2-P3-Cl3	108.31(9)	C7-C8-C9	105.4(2)	N9-P4-N11	111.39(8)	N12-N11-P4	122.39(12)	N5-C3-C4	119.95(16)
N2-P3-Cl4	108.76(9)	N5-C9-C8	112.9(2)	N9-P4-N8	118.34(8)	C21-N11-P4	122.50(13)	C2-C3-N5	106.18(16)
N3-P3-Cl3	109.03(9)	**Compound 5**		Cl2-P3-Cl1	101.79(3)	C21-N11-N12	111.95(15)	C2-C3-C4	133.86(16)

N3-P3-Cl4	109.17(8)	**Atoms**	**Angle/º**	N3-P3-Cl2	108.32(7)	N14-N13-P5	121.12(12)	C27-C22-C21	120.31(16)
N3-P3-N2	118.88(10)	O4-P5-N13	99.01(7)	N3-P3-Cl1	109.51(7)	N14-N13-C30	112.22(15)	C27-C22-C23	117.38(17)
C1-O1-P1	130.49(15)	O4-P5-N10	110.60(8)	N3-P3-N2	118.38(9)	C30-N13-P5	123.51(13)	C23-C22-C21	122.29(17)
P1-N1-P2	122.84(12)	N10-P5-N13	108.14(9)	N2-P3-Cl2	108.98(7)	P6-N8-P4	121.30(10)	C22-C27-O3	120.01(16)
P3-N2-P2	120.46(12)	N9-P5-O4	107.48(8)	N2-P3-Cl1	108.59(7)	P3-N3-P1	121.10(10)	C26-C27-O3	117.08(16)
P3-N3-P1	122.54(12)	N9-P5-N13	111.89(8)	O2-P2-N7	99.73(7)	P3-N2-P2	121.07(10)	C26-C27-C22	122.86(17)
N5-N4-P1	120.29(15)	N9-P5-N10	118.05(8)	O2-P2-N2	110.55(8)	C19-N12-N11	103.56(15)	N11-C21-C22	120.19(16)
C7-N4-P1	127.91(16)	Cl3-P6-Cl4	100.35(4)	N2-P2-N7	108.74(9)	P6-N10-P5	121.60(10)	C20-C21-N11	106.40(16)
C7-N4-N5	111.60(18)	N8-P6-Cl4	110.26(7)	C1-N4-N5	103.83(15)	P5-N9-P4	120.82(10)	C20-C21-C22	133.40(17)
C9-N5-N4	103.76(19)	N8-P6-Cl3	108.79(7)	P2-N1-P1	121.54(10)	C10-N6-N7	103.21(16)	C13-C18-O2	120.84(16)

Table S5. Bond angles of compounds **3** and **5**

Compound 5		**Compound 5**		**Compound 6**		**Compound 6**		**Compound 6**	
Atoms	**Angle/º**	**Atoms**	**Angle/º**	**Atoms**	**Angle/º**	**Atoms**	**Angle/º**	**Atoms**	**Angle/º**
C17-C18-O2	116.77(17)	C27-C26-C25	118.25(19)	N2-P2-O2	108.23(10)	C23-C22-C27	118.1(2)	C16-C17-C18	105.6(2)
C17-C18-C13	122.35(17)	C32-C33-C34	120.35(18)	N2-P2-N6	108.93(10)	N6-C16-C15	118.6(2)	C7-C8-C9	106.3(2)
C31-C36-O4	120.76(16)	C14-C15-C16	120.56(19)	N2-P2-N1	118.33(10)	C17-C16-N6	105.8(2)	N5-C9-C8	112.6(2)
C35-C36-O4	116.92(16)	C30-C29-C28	104.77(18)	C10-O2-P2	122.30(15)	C17-C16-C15	135.5(2)	C4-C5-C6	120.1(3)
C35-C36-C31	122.24(17)	C35-C34-C33	120.30(19)	C1-O1-P1	124.02(15)	C6-C1-O1	120.6(2)	C13-C14-C15	120.5(3)
C36-C31-C30	119.93(16)	C17-C16-C15	119.97(19)	N9-N8-P3	120.39(15)	C2-C1-O1	116.2(2)	C13-C12-C11	120.3(3)
C36-C31-C32	117.77(17)	C26-C25-C24	120.4(2)	C19-N8-P3	127.76(16)	C2-C1-C6	123.1(3)	C1-C2-C3	118.4(3)
C32-C31-C30	122.30(17)	N14-C28C29	113.58(19)	C19-N8-N9	111.12(18)	N4-C7-C6	119.1(2)	C4-C3-C2	120.5(3)
N13-C30-C31	119.82(16)	C23-C24-C25	120.4(2)	N5-N4-P1	121.16(16)	C8-C7-N4	105.1(2)	C25-C26-C27	120.3(3)
C29-C30-N13	106.41(17)	**Compound 6**		N5-N4-C7	112.35(19)	C8-C7-C6	135.7(3)	C25-C24-C23	119.5(3)
C29-C30-C31	133.77(17)	**Atoms**	**Angle/º**	C7-N4-P1	124.42(16)	C10-C15-C16	120.6(2)	C14-C13-C12	120.9(3)
N4-C1-C2	112.81(17)	O1-P1-N4	98.80(10)	C21-N9-N8	105.04(18)	C10-C15-C14	117.2(2)	C26-C25-C24	120.7(3)
C21-C20-C19	104.94(16)	N1-P1-O1	108.01(10)	N7-N6-P2	122.53(15)	C14-C15-C16	122.2(2)	C3-C4-C5	121.0(3)

C6-C5-C4	120.56(18)	N1-P1-N4	111.14(10)	C16-N6-P2	125.26(16)	C1-C6-C7	120.9(2)		
C3-C2-C1	105.13(16)	N1-P1-N3	117.94(11)	C16-N6-N7	112.16(18)	C1-C6-C5	117.0(3)		
C9-C8-C7	118.35(18)	N3-P1-O1	109.64(10)	P1-N1-P2	121.29(12)	C5-C6-C7	122.2(3)		
C8-C7-C6	120.25(18)	N3-P1-N4	109.58(10)	P2-N2-P3	121.70(13)	C19-C20-C21	106.1(2)		
C34-C35-C36	118.77(18)	N8-P3-Cl1	100.58(7)	P3-N3-P1	121.08(12)	C15-C10-O2	120.0(2)		
C18-C17-C16	118.9(2)	N2-P3-Cl1	110.47(8)	C18-N7-N6	103.5(2)	C11-C10-O2	116.8(2)		
N12-C19-C20	113.07(17)	N2-P3-N8	107.03(10)	C9-N5-N4	103.6(2)	C11-C10-C15	123.2(2)		
C12-C11-C10	105.14(17)	N2-P3-N3	118.10(11)	N9-C21-C22	120.2(2)	N7-C18-C17	112.9(2)		
C5-C6-C7	120.52(18)	N3-P3-Cl1	108.63(8)	N9-C21-C20	110.8(2)	O3-C27-C22	123.1(2)		
C33-C32-C31	120.52(18)	N3-P3-N8	110.61(10)	C20-C21C22	129.1(2)	O3-C27-C26	116.9(3)		
N6-C10-C11	113.31(18)	O2-P2-N6	99.17(9)	C20-19-N8	107.0(2)	C22-C27-C26	120.0(3)		
C15-C14-C13	120.6(2)	O2-P2-N1	110.35(10)	C27-C22-C21	121.7(2)	C10-C11-C12	118.0(3)		
C24-C23-C22	120.64(19)	N1-P2-N6	110.11(10)	C23-C22-C21	120.2(2)	C24-C23-C22	121.5(3)		

Table S6. Bond angles of compounds **5** and **6**

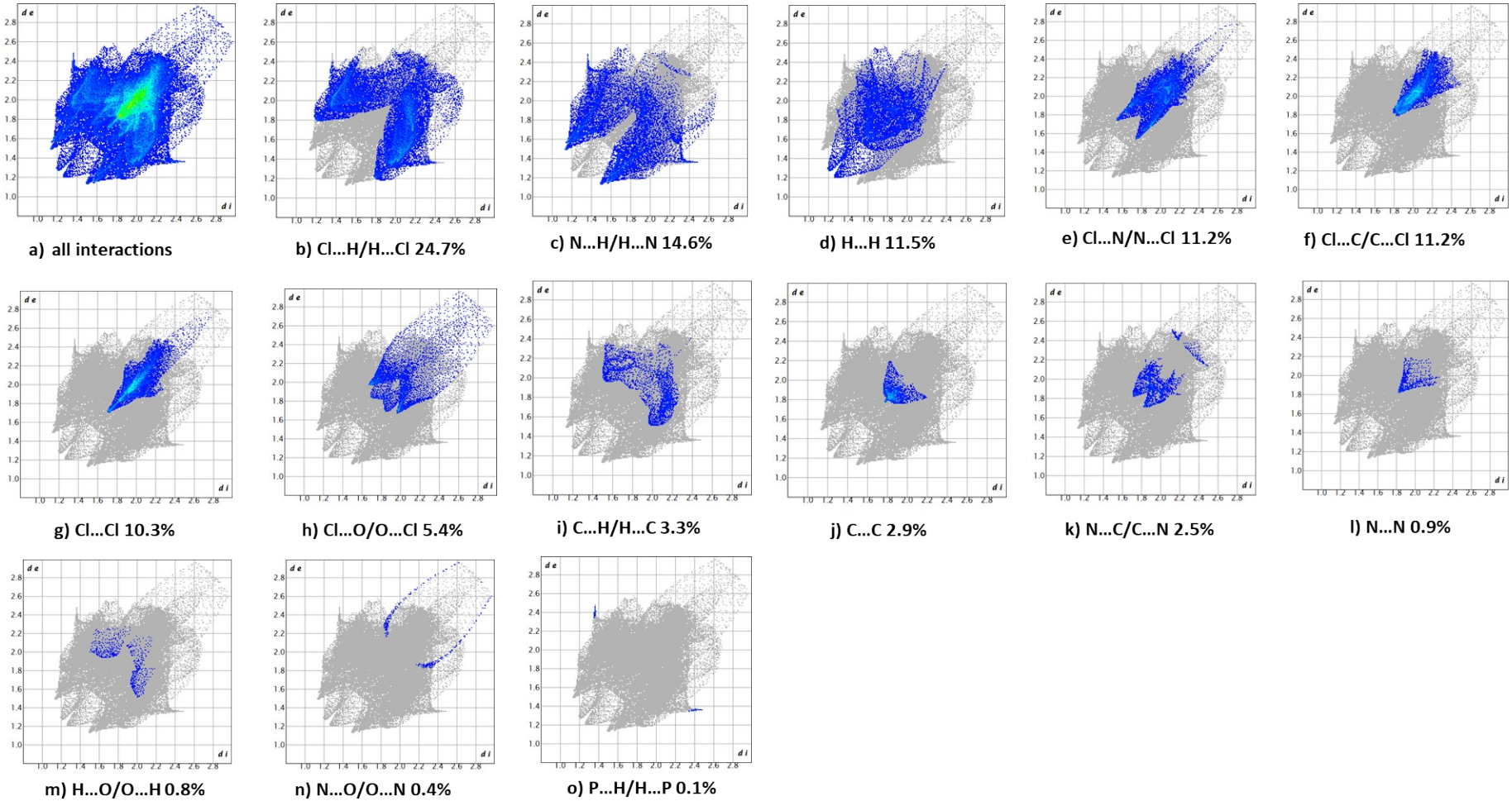

Figure S13. The full two-dimensional fingerprint plots of compound **3** showing (a) all interactions, and delineated into (b) H ... Cl/Cl ... H (c) H ... N/N … H, (d) H…H (e) Cl ...N/N …Cl, (f) C...Cl/Cl ...C, (g) Cl ... Cl, (h) Cl…O/O…Cl (i) H ... C/C ... H, (j) C…C (k) N…C/C…N (l) N…N (m) H…O/O…H (n) N…O/O…N and (o) P … H/H … P interactions. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface contacts.

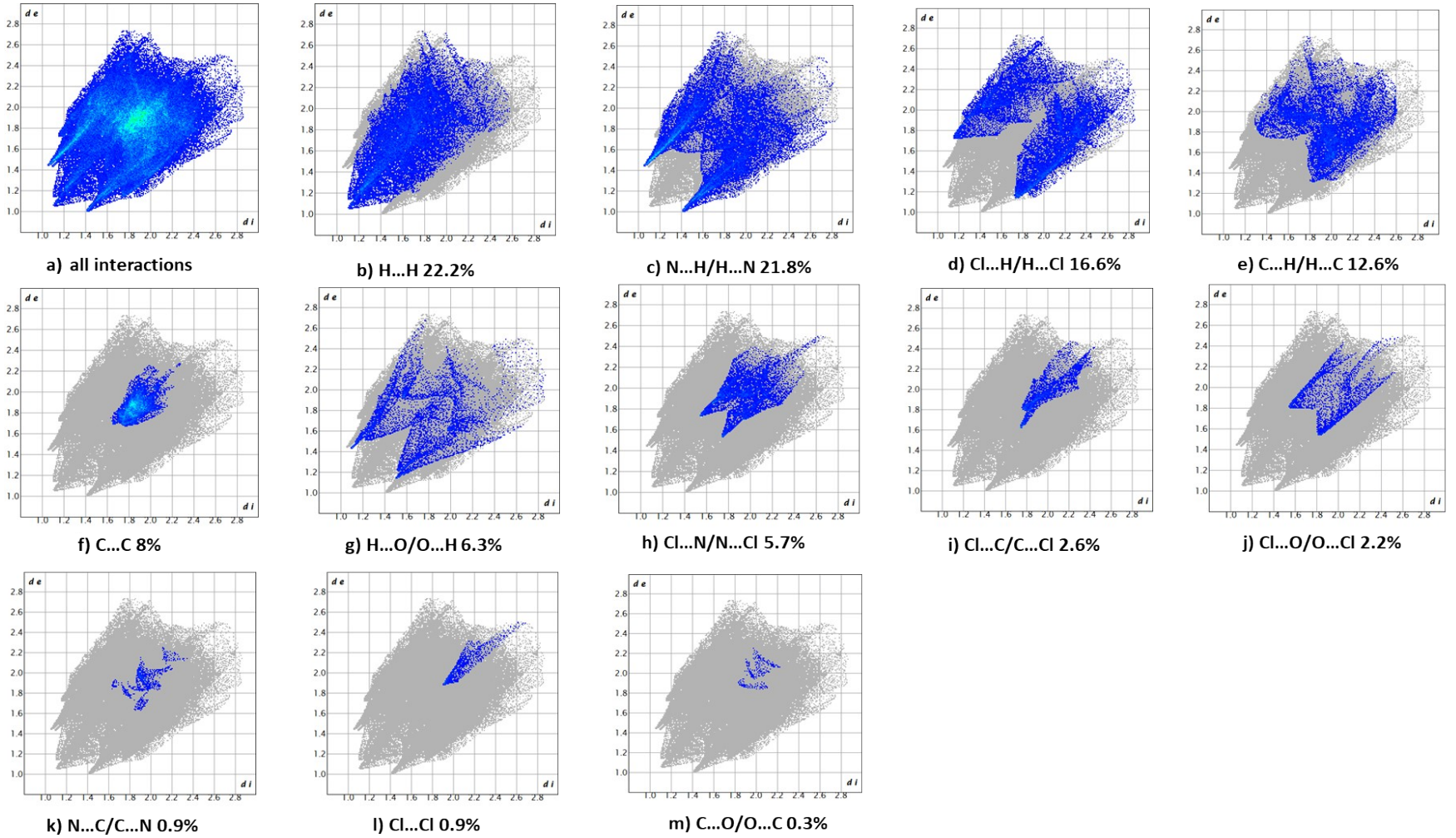

Figure S14. The full two-dimensional fingerprint plots of compound **5** showing (a) all interactions, and delineated into (b) H…H (c) H ... N/N … H, (d) H ... Cl/Cl … H (e) H ... C/C ... H, (f) C…C, (g) H…O/O…H (h) Cl ...N/N …Cl, (i) C...Cl/Cl ...C, (j) Cl…O/O…Cl (k) N…C/C…N (l) Cl ... Cl, (m) C…O/O…C. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface contacts.

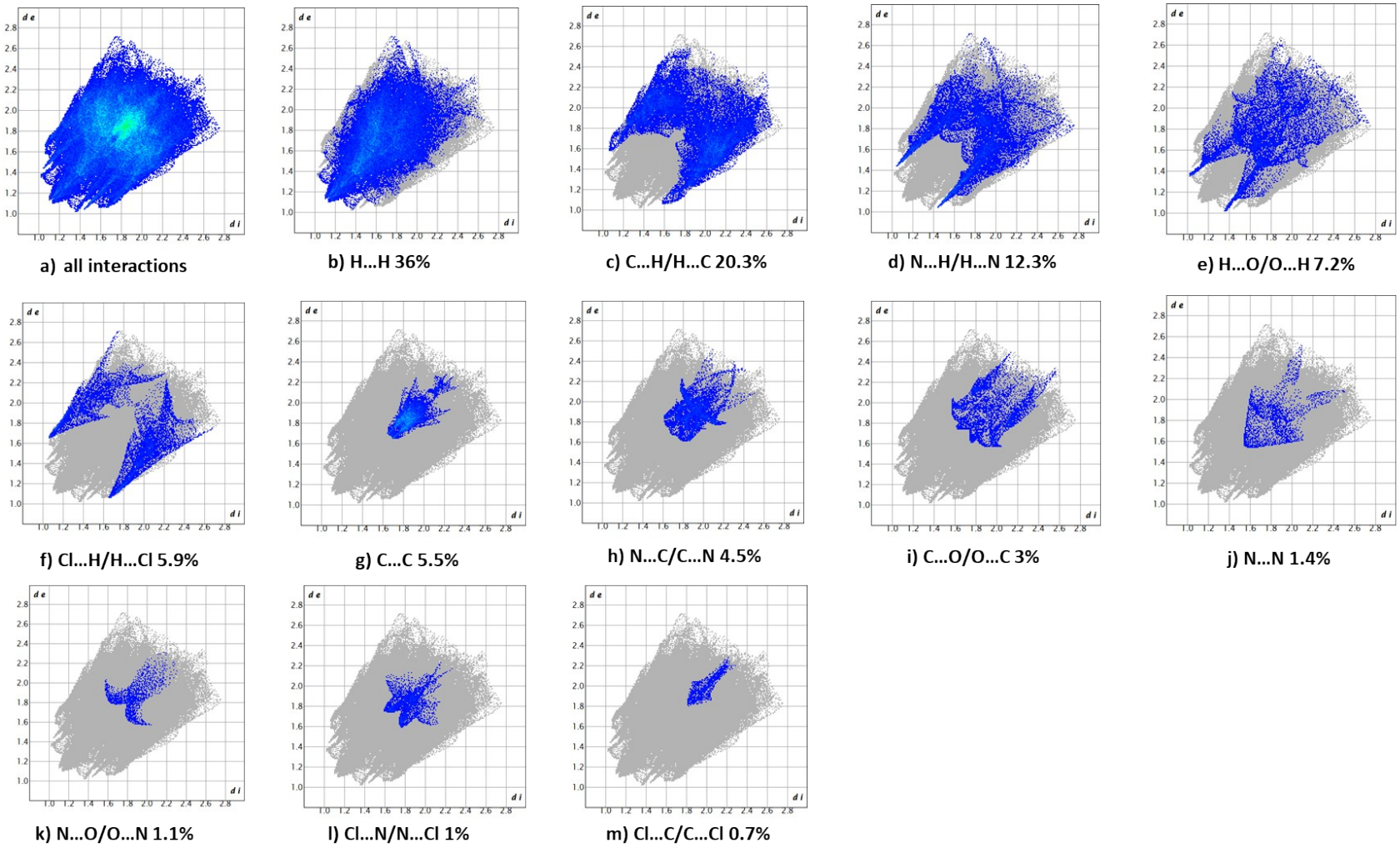

Figure S15. The full two-dimensional fingerprint plots of compound **6** showing (a) all interactions, and delineated into (b) H…H (c) H ... C/C ... H, (d) H ... N/N … H, (e) H…O/O…H, (f) H ... Cl/Cl … H, (g) C…C, (h) N…C/C…N, (i) C…O/O…C, (j) N…N, (k) N…O/O…N, (l) Cl...N/N …Cl, (m) C...Cl/Cl ...C. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface contacts.

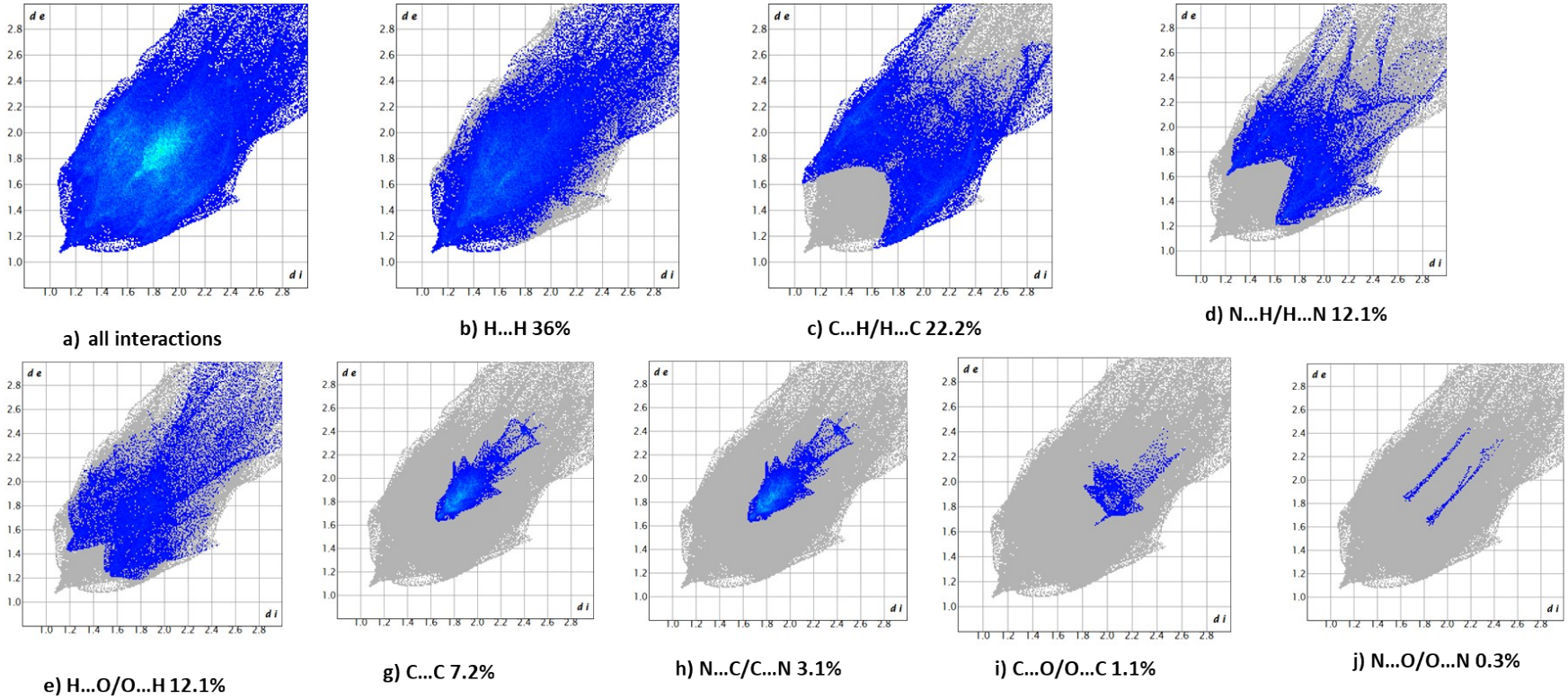

Figure S16. The full two-dimensional fingerprint plots of compound **7** showing (a) all interactions, and delineated into (b) H…H (c) H...C/C...H, (d) H... N/N…H, (e) H…O/O…H, (g) C…C, (h) N…C/C…N, (i) C…O/O…C, (j) N…O/O…N. The d_i and d_e values are the closest internal and external distances (in Å) from given points on the Hirshfeld surface contacts.

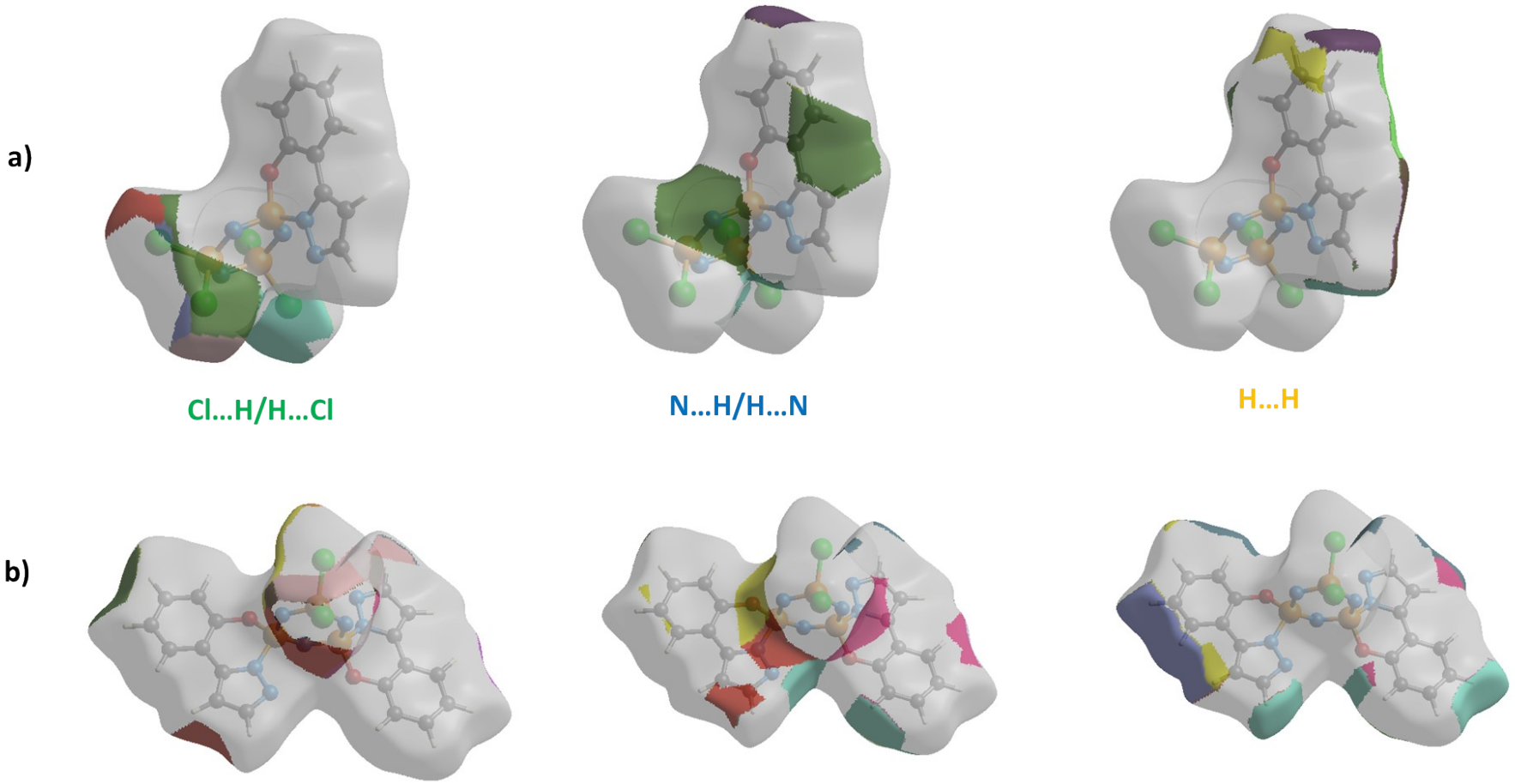

Figure S17. The Hirshfeld surface representations with the function d_{norm} plotted onto the surface for Cl…H/H…Cl, N…H/H…N and H…H **a)** for compound **3 b)** for compound **5**

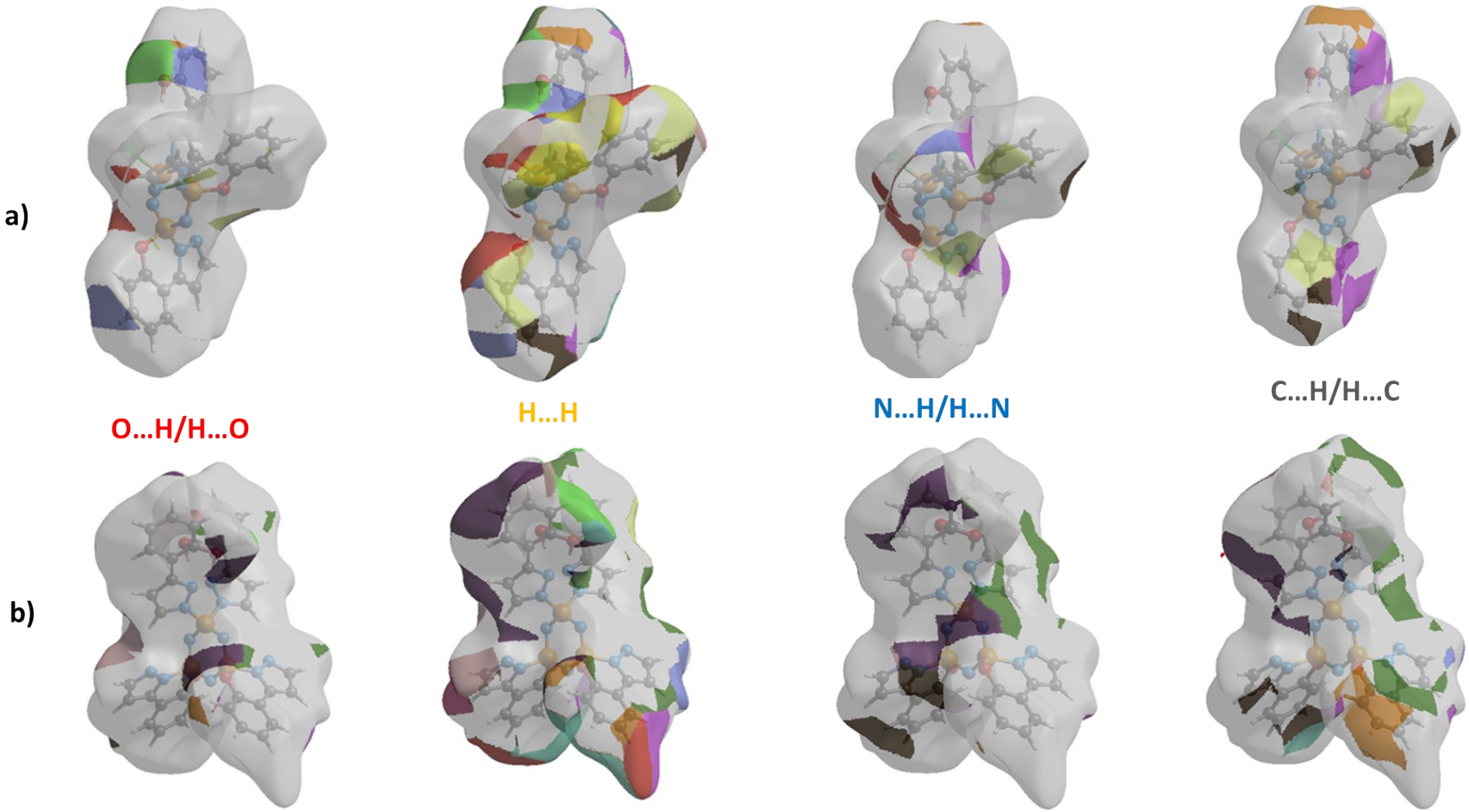

Figure S18. The Hirshfeld surface representations with the function d_{norm} plotted onto the surface for O…H/H…O, H…H, N…H/H…N and C…H/H…C **a)** for compound **6 b)** for compound **7**