Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information

Table S1 - Atomic point charges (in atomic charge units percentage, a.c.u.%) for molecules Cp_2MX_2 (M = Ti, Zr; X = F, I. M = Mo, W; X = H).

Compound	Cp_2TiF_2	Cp_2ZrF_2	Cp_2TiI_2	Cp_2ZrI_2	Cp_2MoH_2	Cp_2WH_2
M	100	118	61	82	48	56
C1	-4	-11	-7	3	4	0
C2	-16	-15	-5	-9	-23	-22
C3	-12	-8	-10	-2	-4	-8
C4	-12	-10	-16	-16	-4	-5
C5	-14	-14	2	-9	-23	-22
C1’	-4	-11	-7	4	4	1
C2’	-16	-15	2	-10	-23	-23
C3’	-11	-8	-16	-17	-4	-5
C4’	-12	-10	-10	-2	-4	-7
C5’	-14	-14	-5	-10	-24	-22
H1	10	12	8	3	6	8
H2	12	10	8	6	11	11
H3	9	7	9	4	11	13
H4	9	7	12	10	11	12
H5	12	9	4	6	11	11
H1’	10	12	8	3	6	7
H2’	12	10	4	7	10	11
H3’’	9	7	12	11	11	12
H4’	9	7	9	4	11	13
H5’	12	9	8	6	11	11
F1	-45	-47	---	---	---	---
F1’	-45	-47	---	---	---	---
I1	---	---	-34	-36	---	---
I1’	---	---	-34	-36	---	---
H1	---	---	---	---	-23	-25
H1’	---	---	---	---	-23	-25

Table S2 - Atomic point charges (in atomic charge units percentage, a.c.u.%) for molecules Cp_2MX_2 (M = Ti, Zr, Hf, V, Nb, Ta, Mo; X = Cl, Br).

Comp,	Cp_2TiCl_2	Cp_2ZrCl_2	Cp_2HfCl_2	Cp_2VCl_2	Cp_2NbCl_2	Cp_2TaCl_2	Cp_2MoCl_2	Cp_2TiBr_2	Cp_2ZrBr_2	Cp_2HfBr_2
M1	73	97	100	61	70	74	54	65	85	91
C1	-8	-2	-3	-7	9	-3	-4	-7	1	-2
C2	-8	-15	-18	-5	-14	-15	-10	-6	-15	-17
C3	-10	-7	-6	-12	5	-2	-4	-9	-8	-5
C4	-11	-12	-5	-11	-5	3	-21	-14	-5	-13
C5	-9	-13	-18	-6	-21	-17	6	-4	-16	-10
C1’	-5	-5	1	-3	7	-4	2	-7	-3	-6
C2’	-9	-10	-17	-5	-11	-2	-5	-7	-17	-8
C3’	-12	-13	-7	-13	-14	-15	-16	-9	-7	-14
C4’	-11	-5	-8	-5	1	3	4	-11	-11	-5
C5’	-10	-15	-15	-14	-19	-20	-19	-7	-14	-13
H1	12	8	8	14	7	10	12	9	6	7
H2	8	11	9	9	10	8	7	9	10	12
H3	10	6	7	12	5	7	11	8	7	5
H4	9	9	5	12	4	2	11	11	6	10
H5	11	9	12	10	8	12	9	7	11	7
H1’	11	9	6	12	7	11	12	10	9	8
H2’	11	7	11	12	10	9	11	7	12	7
H3’’	9	10	4	10	10	7	11	10	8	10
H4’	11	5	7	11	7	6	8	9	9	5
H5’	10	11	8	10	10	8	10	9	11	10
Cl1	-40	-42	-42	-44	-43	-42	-44	---	---	---
Cl1’	-40	-42	-42	-44	-42	-42	-44	---	---	---
Br1	---	---	---	---	---	---	---	-36	-39	-38
Br1’	---	---	---	---	---	---	---	-36	-40	-38
M2	75	97	100	59	71	71	48	66	82	90
C6	-9	-5	-9	-4	-2	0	-7	-8	-1	-1
C7	-9	-11	-12	-6	-5	-1	4	-6	-13	-13
C8	-10	-12	-10	-15	-13	-17	-14	-11	-11	-9
C9	-12	-7	-11	-4	-1	-5	-2	-11	-7	-10
C10	-8	-15	-11	-10	-20	-10	-8	-5	-14	-8
C6’	-8	-5	-4	-3	-11	-7	5	-9	1	-2
C7’	-8	-15	-15	-8	3	8	-1	-7	-16	-9
C8’	-13	-8	-16	-14	-13	-18	-21	-13	-5	-14
C9’	-10	-12	-3	-3	-1	3	5	-10	-8	-4
C10’	-10	-11	-15	-14	-11	-22	-22	-6	-14	-13
H6	12	9	10	13	11	9	14	11	9	5
H7	11	8	11	9	10	7	7	9	8	9
H8	9	9	7	12	8	9	11	8	10	6
H9	11	6	9	9	8	9	10	11	6	8
H10	8	12	8	9	10	6	7	7	11	6
H6’	12	9	10	13	10	11	10	11	7	6
H7’	9	12	9	12	9	7	11	7	11	6
H8’	11	6	11	11	7	7	10	12	6	9
H9’	9	9	5	10	7	7	8	9	9	5
H10’	11	8	11	10	9	10	11	9	8	8
Cl2	-40	-42	-42	-44	-43	-42	-43	---	---	---
Cl2’	-41	-42	-42	-44	-43	-42	-44	---	---	---
Br2	---	---	---	---	---	---	---	-36	-39	-38
Br2’	---	---	---	---	---	---	---	-37	-39	-38

Table S3 – Intermolecular contact parameters in Cp_2TiF_2.

Chain interactions				
	C···F (Å)	H···F (Å)	C-H···F (°)	H···F-M (°)
C3-H3···F	3.308	2.481	147.7	123.5
C3'-H3'···F	3.308	2.481	147.7	123.5
C4-H4···F'	3.323	2.488	144.5	125.9
C4'-H4'...F'	3.323	2.488	144.5	125.9
Plane-plane interactions				
	C···F (Å)	H···F (Å)	C-H···F (°)	H···F-M (°)
C4-H4···F	3.349	2.766	120.4	119.8
C4'-H4'···F	3.349	2.766	120.4	119.8
C3-H3···F'	3.416	2.864	118.0	119.0
C3'-H3'···F'	3.416	2.864	118.0	119.0
C-H···π interactions*				
C(1)-H(1)···π	D_{pln} = 2.708 Å	D_{cp} = 0.266 Å	α = 141,1º	

* The criteria recently developed by Nishio and co-workers (see ref.19) to describe this type of interactions will be adopted in the current manuscript, due to their suitability to the geometry of the type of interactions reported herein:

D_{pln} – distance from the H atom to the plane of the π ring system

D_{cp} – distance between the projection of the hydrogen atom on the ring plane and the π system centroid

α – angle between the C-H bond and the projection of the hydrogen atom on the ring plane

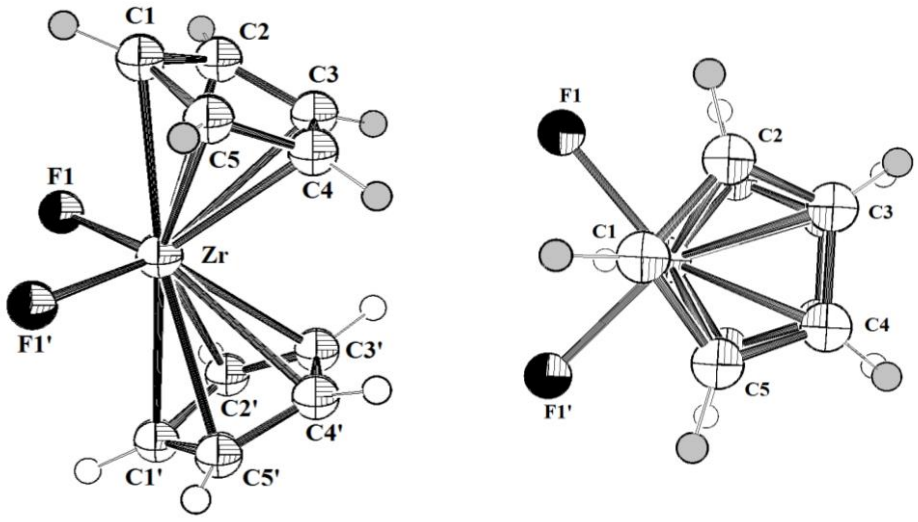

Figure S1. ORTEP diagram, drawn with 50% probability ellipsoids, showing the atomic labelling scheme for FDCPZR (Cp_2ZrF_2). The molecule was labelled clockwise with the bonds that lay in the middle of the F-Zr-F angle designated as C(1)-H(1) and C(1')-H(1'). Halogen atoms have been coloured in black, hydrogen atoms of the upper ring in grey and all the atoms of the lower ring identified by a ' superscript.

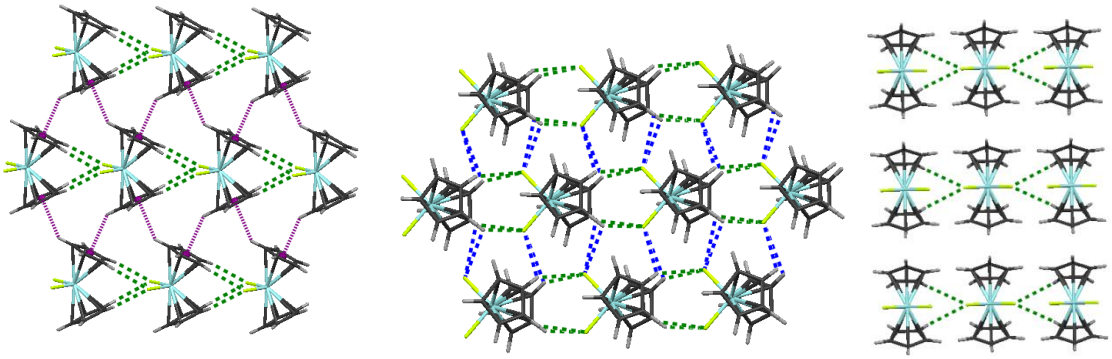

Figure S2 – Supramolecular arrangement of Cp_2ZrF_2: planes of chains formed by C-H···F interactions (in green) and C-H···π contacts (in purple) (left); interaction between these planes by perpendicular C-H···F interactions (in blue): top (centre) and front (right) views.

Table S4 – Intermolecular contact parameters in Cp_2ZrF_2.

Chain interactions				
	C···F (Å)	H···F (Å)	C-H···F (°)	H···F-M (°)
C3-H3···F	3.431	2.582	149.0	120.8
C3'-H3'···F	3.431	2.582	149.0	120.8
C4-H4···F'	3.431	2.567	151.5	120.3
C4'-H4'...F'	3.431	2.567	151.5	120.3
Plane-plane interactions				
	C···F (Å)	H···F (Å)	C-H···F (°)	H···F-M (°)
C4-H4···F	3.469	2.943	116.2	117.7
C4'-H4'···F	3.469	2.944	116.2	117.7
C3-H3···F'	3.487	2.944	117.6	117.8
C3'-H3'···F'	3.487	2.944	117.6	117.6
C-H···π interactions				
C(1)-H(1)···π	D_{pln} = 2.726 Å	D_{cp} = 0.130 Å	α = 153.3º	

Table S5 – Intermolecular contact parameters in Cp_2TiCl_2.

Chain interactions				
	C···Cl (Å)	H···Cl (Å)	C-H···Cl (°)	H···Cl-M (°)
C8-H8···Cl1	3.769	3.102	128.7	121.4
C8'-H8'···Cl1	3.743	2.795	175.5	104.6
C9-H9···Cl1'	3.667	2.724	171.6	96.3
C9'-H9'···Cl1'	3.574	2.921	126.9	138.1
C3-H3···Cl2	3.770	2.854	162.4	100.9
C3-H3···Cl2'	3.769	3.133	125.9	93.3
C3'-H3'··.Cl2	3.646	2.833	144.3	118.2
C4'-H4'···Cl2'	3.771	2.857	161.9	103.7
Plane-plane interactions				
	C···Cl (Å)	H···Cl (Å)	C-H···Cl (°)	H···Cl-M (°)
C2-H2···Cl1	3.799	3.023	139.8	113.4
C3'-H3'···Cl1	3.787	3.100	130.5	144.2
C10-H10··Cl1'	3.640	2.800	147.9	120.4
C8-H8···Cl2	3.897	3.082	144.9	131.0
C7'-H7'···Cl2	3.685	2.941	136.2	106.3
C4-H4···Cl2'	3.746	2.881	151.9	116.8
C5'-H5'···Cl2'	3.824	3.193	125.5	116.8
C-H···π interactions				
C10'-H10'···π_{II}	D_{pln} = 2.798 Å	D_{cp} = 1.226 Å	α = 122.9°	
C7-H7···π_{I}	D_{pln} = 2.654 Å	D_{cp} = 1.917 Å	α = 118.4º	
Halogen interactions				
Cl1···Cl2 (Å)	Ti1-Cl1··Cl2 (°)	Cl2··Cl1-Ti1 (°)		
3.974	168.0	168.0		

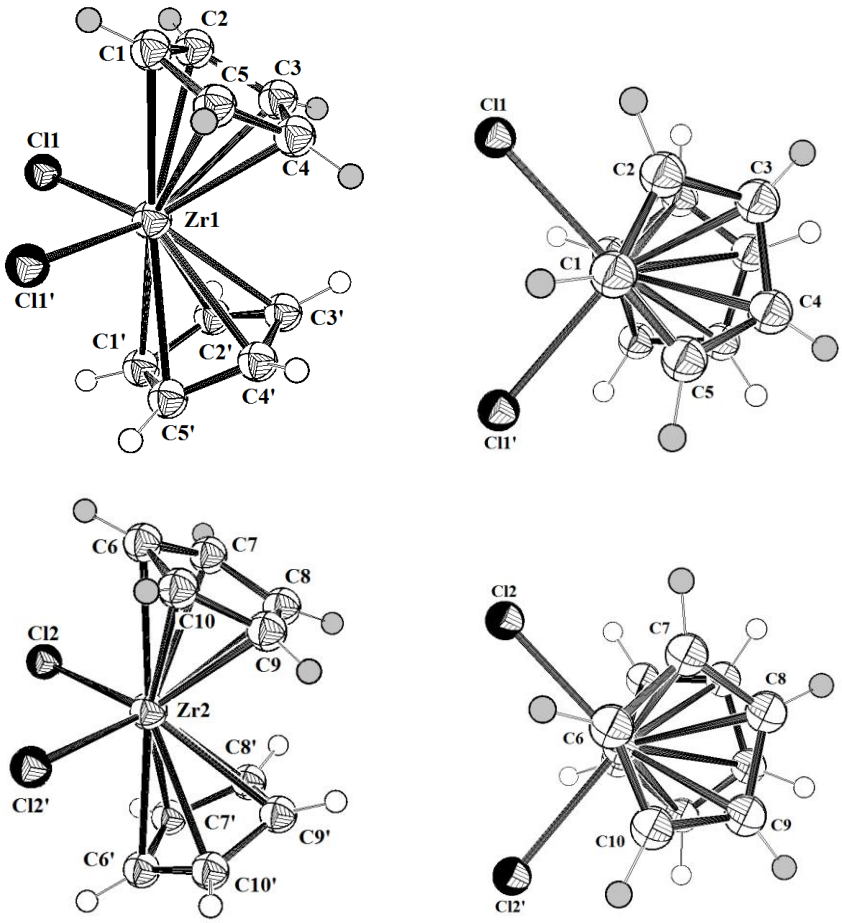

Figure S3. ORTEP diagram, drawn with 50% probability ellipsoids, showing the atomic labelling scheme for the two types of molecules of CPDCZR04 (Cp_2ZrCl_2) (type A molecules on top, type B below).

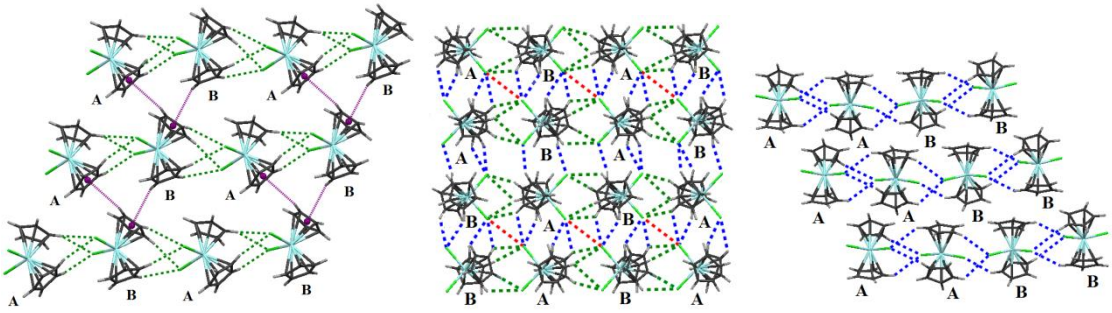

Figure S4 – Supramolecular arrangement of Cp_2ZrCl_2. Planes of chains formed by C-H···Cl interactions (in green) and C-H···π contacts (in purple) (left). Interaction between these planes by C-H···Cl interactions (in blue) and Cl···Cl interactions (in red): top (centre) and front (right) views.

Table S6 – Intermolecular contact parameters in Cp_2ZrCl_2.

Chain interactions				
	C···Cl (Å)	H···Cl (Å)	C-H···Cl (°)	H···Cl-M (°)
C8-H8···Cl1	3.820	2.873	175.0	102.0
C8'-H8'···Cl1	3.843	3.135	132.7	117.2
C9-H9···Cl1'	3.656	2.986	128.6	135.1
C9'-H9'···Cl1'	3.737	2.793	173.1	95.7
C3-H3···Cl2	3.713	2.855	150.8	112.9
C3'-H3'··.Cl2	3.858	2.936	164.0	99.8
C4-H4···Cl2'	3.858	2.947	125.9	93.3
C3'-H3'···Cl2'	3.771	2.857	161.9	103.7
Plane-plane interactions				
	C···Cl (Å)	H···Cl (Å)	C-H···Cl (°)	H···Cl-M (°)
C2'-H2'···Cl1	3.815	3.068	136.6	111.6
C3-H3···Cl1	3.861	3.195	128.6	142.8
C10'-H10'···Cl1'	3.660	2.866	141.8	118.9
C8'-H8'···Cl2	3.958	3.150	143.9	130.5
C7-H7···Cl2	3.726	2.998	134.5	106.6
C4'-H4'···Cl2'	3.849	2.997	150.0	115.3
C5-H5···Cl2'	3.880	3.312	120.4	114.4
C-H···π interactions				
C10-H10···π_{II}	D_{pln} = 2.835 Å	D_{cp} = 1.188 Å	α = 117.1°	
C7'-H7'···π_{I}	D_{pln} = 2.751 Å	D_{cp} = 1.828 Å	α = 118.1º	
Halogen interactions				
Cl1···Cl2 (Å)	Zr1-Cl1···Cl2 (°)	Cl1···Cl2-Zr2 (°)		
3.850	166.5	167.3		

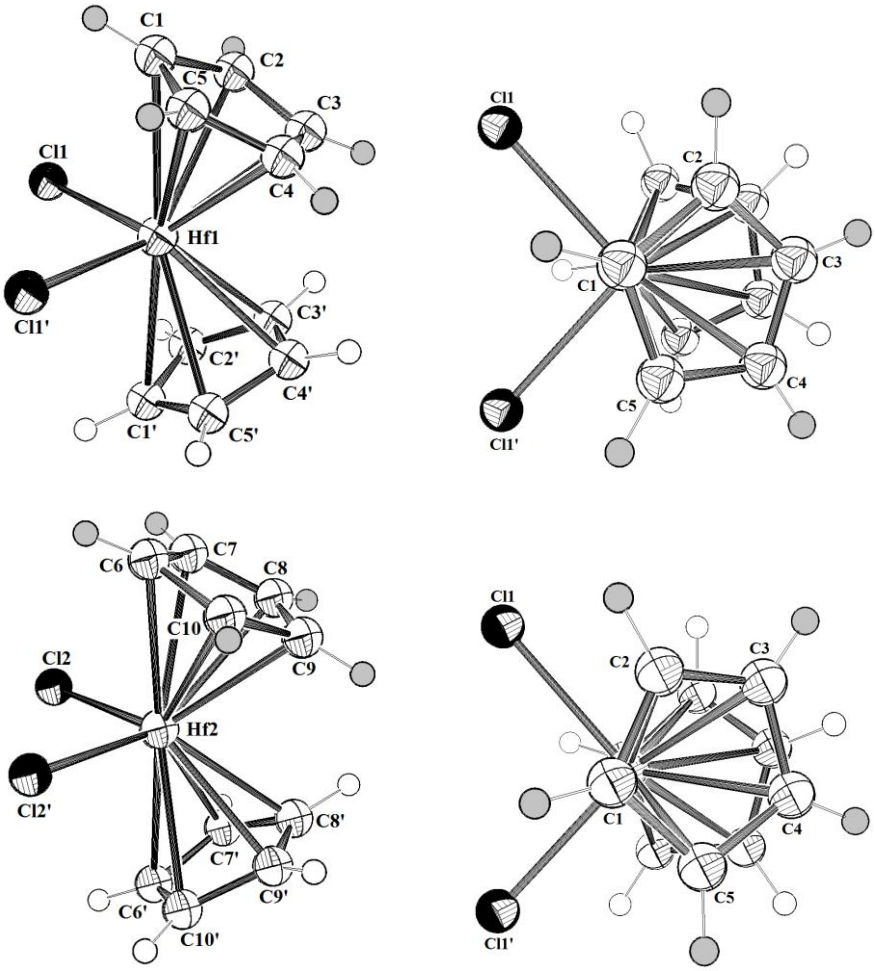

Figure S5. ORTEP diagram, drawn with 50% probability ellipsoids, showing the atomic labelling scheme for the two types of molecules of KOKPEF (Cp_2HfCl_2) (type A molecules on top, type B below).

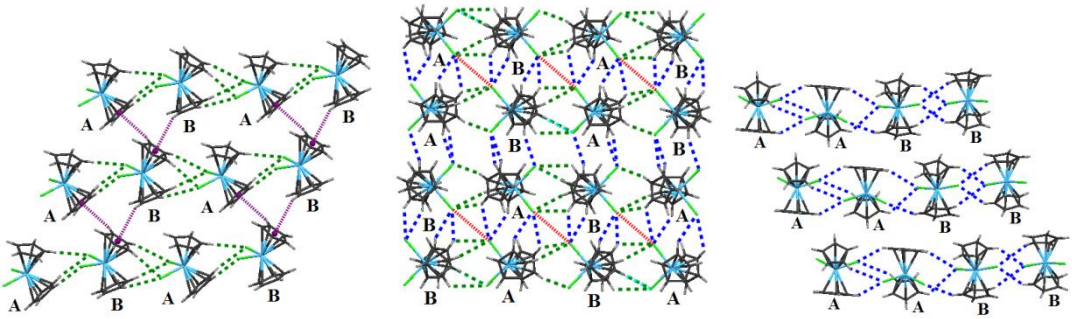

Figure S6 – Supramolecular arrangement of Cp_2HfCl_2. Planes of chains formed by C-H···Cl interactions (in green) and C-H···π contacts (in purple) (left). Interaction between these planes by C-H···Cl interactions (in blue) and Cl···Cl interactions (in red): top (centre) and front (right) views.

Table S7 – Intermolecular contact parameters in Cp_2HfCl_2.

Chain interactions				
	C···Cl (Å)	H···Cl (Å)	C-H···Cl (°)	H···Cl-M (°)
C8-H8···Cl1	3.892	3.202	131.1	117.7
C8'-H8'···Cl1	3.854	2.912	171.7	102.0
C9-H9···Cl1'	3.758	2.809	176.7	97.4
C9'-H9'···Cl1'	3.753	3.123	125.3	136.1
C3-H3···Cl2	3.912	2.977	168.5	103.2
C3'-H3'···Cl2	3.795	2.968	146.2	115.1
C4'-H4'···Cl2'	3.890	2.964	165.3	103.0
Plane-plane interactions				
	C···Cl (Å)	H···Cl (Å)	C-H···Cl (°)	H···Cl-M (°)
C2-H2···Cl1	3.880	3.150	134.9	110.3
C3'-H3'···Cl1	3.955	3.247	132.8	139.4
C10-H10···Cl1'	3.714	2.892	145.4	119.5
C8-H8···Cl2	4.047	3.240	144.0	129.1
C7'-H7'···Cl2	3.797	3.007	141.5	107.8
C4-H4···Cl2'	3.913	3.084	146.7	118.6
C5'-H5'···Cl2'	3.938	3.313	125.2	115.3
C-H···π interactions				
C7-H7···π_{II}	D_{pln} = 2.747 Å	D_{cp} = 1.912 Å	α = 119.9°	
C10'-H10'···π_{I}	D_{pln} = 2.873 Å	D_{cp} = 1.325 Å	α = 116.3º	
Halogen interactions				
Cl1···Cl2 (Å)	Hf1-Cl1···Cl2 (°)	Cl1···Cl2-Hf2 (°)		
3.944	168.6	168.9		

Table S8 - Intermolecular contact parameters in Cp_2VCl_2.

Chain interactions				
	C···Cl (Å)	H···Cl (Å)	C-H···Cl (°)	H···Cl-M (°)
C4-H4···Cl1	3.604	2.743	154.3	128.3
C4'-H4'···Cl1	3.650	2.863	143.2	90.5
C3-H3···Cl1'	3.679	2.830	150.8	127.7
C4'-H4'···Cl1'	3.666	2.859	145.8	90.7
C9-H9···Cl2	3.765	2.852	167.3	92.4
C9'-H9'···Cl2	3.912	3.081	149.6	103.8
C9-H9···.Cl2'	3.744	3.124	125.8	86.1
C9'-H9'···Cl2'	3.860	3.063	144.7	104.6
Chain-chain interactions				
	C···Cl (Å)	H···Cl (Å)	C-H···Cl (°)	H···Cl-M (°)
C6-H6···Cl1'	3.600	2.941	128.8	98.3
C1'-H1'···Cl2	3.906	3.041	155.5	95.1
Plane-plane interactions				
	C···Cl (Å)	H···Cl (Å)	C-H···Cl (°)	H···Cl-M (°)
C2-H2···Cl1	3.561	2.978	122.1	99.1
C3-H3···Cl1	3.630	3.118	116.5	145.1
C5-H5···Cl1'	3.673	3.103	121.2	102.9
C4'-H4'...Cl1'	3.755	2.928	148.8	122.2
C10-H10···Cl2	3.736	2.951	142.9	89.0
C7'-H7'···Cl2	3.932	3.011	170.6	153.0
C8-H8···Cl2'	3.646	2.740	164.8	127.3
C8'-H8'···Cl2'	3.568	2.671	162.6	98.5
C-H···π interactions				
C3-H3···π_{II}	D_{pln} = 2.709 Å	D_{cp} = 2,544 Å	α = 116.6º	
C1-H1···π_{II}	D_{pln} = 2.866 Å	D_{cp} = 3.190	α = 93.3°	
Halogen interactions				
Cl2'···Cl2' (Å)	V2-Cl2'···Cl2' (°)	Cl2'···Cl2'-V2 (°)		
3.699	165.8	165.8		

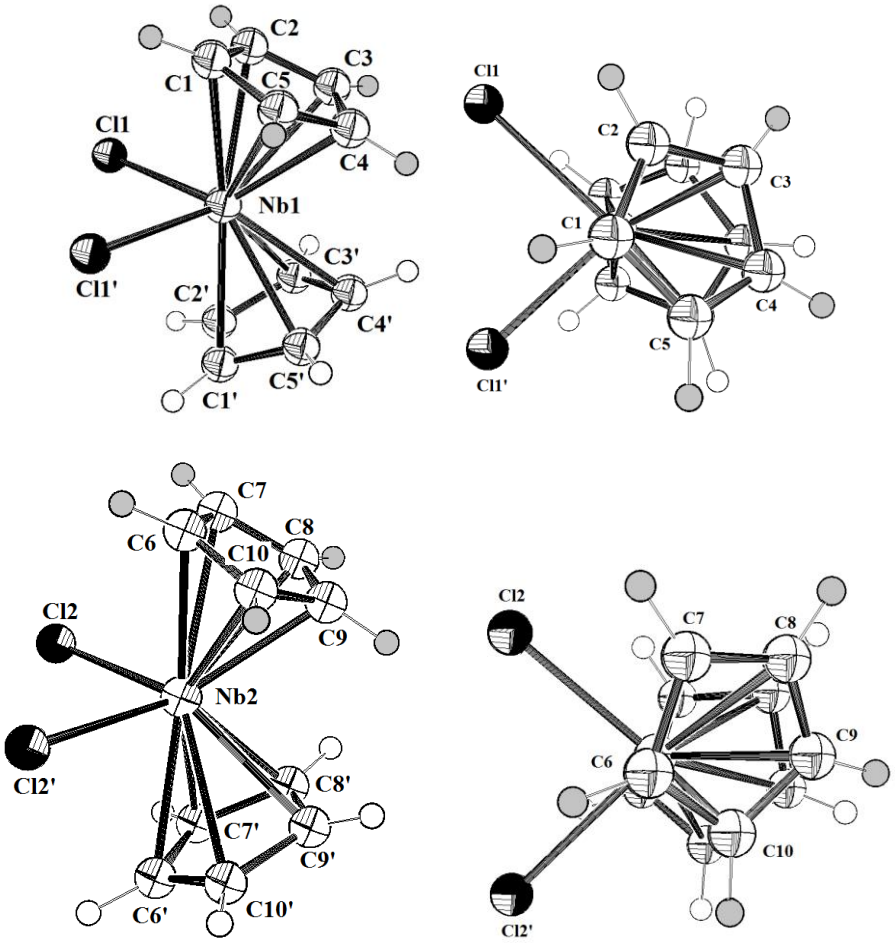

Figure S7. ORTEP diagram, drawn with 50% probability ellipsoids, showing the atomic labelling scheme for the two types of molecules of CPCLNB (Cp_2NbCl_2) (type A molecules on top, type B below).

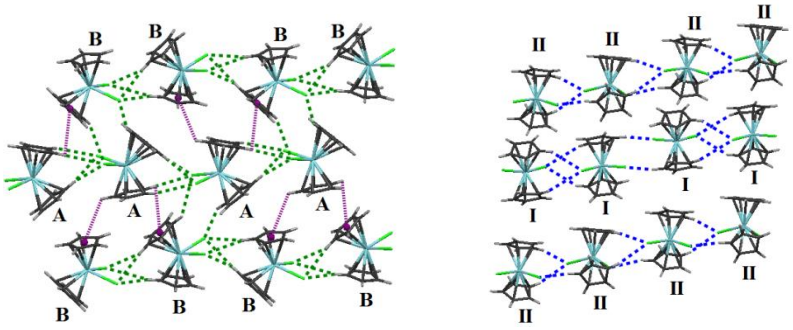

Figure S8 – Primary supramolecular arrangement of Cp_2NbCl_2: planes of chains formed by C-H···Cl interactions (in green) and C-H···π contacts (in purple) between Type I and Type II molecules (left). Front view of secondary supramolecular arrangements of Cp_2NbCl_2 showing lateral C-H···Cl interactions between those planes (right).

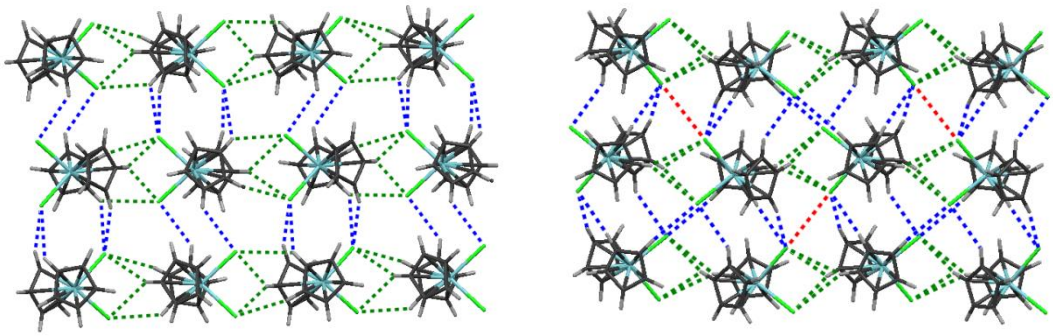

Figure S9 – Top views of secondary supramolecular arrangements between Cp_2NbCl_2 chains formed by type A (left) and type B molecules (right), involving C-H···Cl interactions (in blue) and Cl···Cl interactions (red).

Table S9 - Intermolecular contact parameters in Cp_2NbCl_2.

Chain interactions				
	C···Cl (Å)	H···Cl (Å)	C-H···Cl (°)	H···Cl-M (°)
C4-H4···Cl1	3.796	2.862	167.9	119.9
C4'-H4'···Cl1	3.736	2.884	149.8	89.2
C3-H3···Cl1'	3.768	3.019	136.7	136.3
C4'-H4'···Cl1'	3.701	2.927	139.5	88.5
C9-H9···Cl2	4.064	3.217	149.1	104.2
C9'-H9'···Cl2	3.856	2.931	165.1	90.1
C9-H9···Cl2'	3.995	3.161	147.6	106.1
C9'-H9'···Cl2'	3.809	3.151	127.9	85.3
Chain-chain interactions				
	C···Cl (Å)	H···Cl (Å)	C-H···Cl (°)	H···Cl-M (°)
C6'-H6'···Cl1	3.738	3.095	126.4	95.7
C2-H2···Cl2	3.935	3.062	153.5	96.9
Plane-plane interactions				
	C···Cl (Å)	H···Cl (Å)	C-H···Cl (°)	H···Cl-M (°)
C3-H3···Cl1	3.877	3.182	131.5	137.6
C3'-H3'···Cl1	3.735	2.890	148.7	120.3
C5-H5···Cl1'	3.680	2.931	136.6	96.2
C7-H7···Cl2	4.090	3.151	170.2	152.5
C10'-H10'···Cl2	3.818	2.972	149.1	90.3
C8-H8···Cl2'	3.687	2.756	166.9	101.2
C8'-H8'···Cl2'	3.764	2.848	162.2	126.7
C-H···π interactions				
C4-H4···π_{II}	D_{pln} = 2.878 Å	D_{cp} = 1.689 Å	α = 93.9º	
C1-H1···π_{II}	D_{pln} = 2.776 Å	D_{cp} = 2.040 Å	α = 118.4°	
Halogen interactions				
Cl2'···Cl2' (Å)	Nb2-Cl2'···Cl2' (°)			
3.723	164.8			

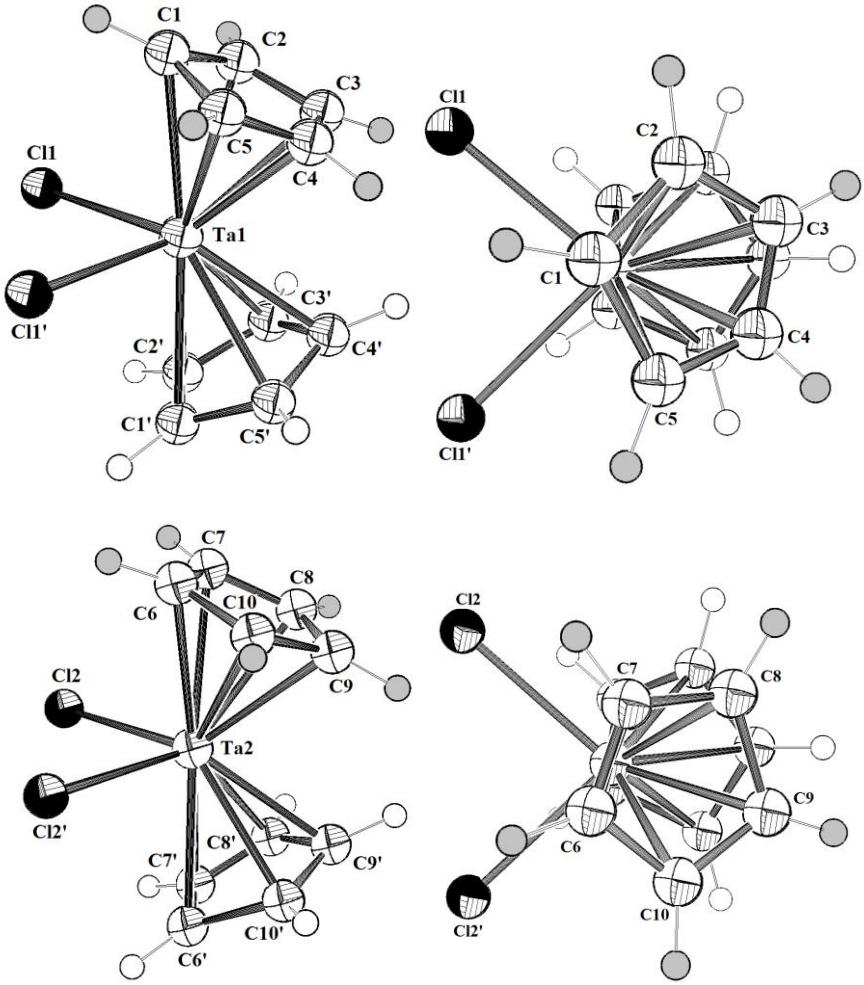

Figure S10. ORTEP diagram, drawn with 50% probability ellipsoids, showing the atomic labelling scheme for the two types of molecules of KOKPIJ (Cp_2TaCl_2) (type A molecules on top, type B below).

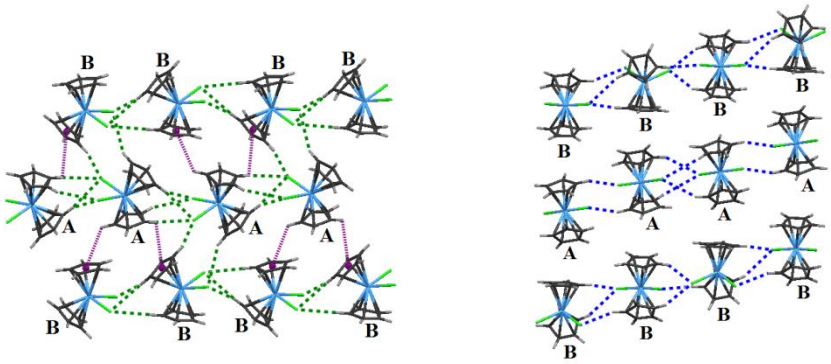

Figure S11 – Primary supramolecular arrangement of Cp_2TaCl_2: planes of chains formed by C-H···Cl interactions (in green) and C-H···π contacts (in purple) between Type I and Type II molecules (left). Front view of secondary supramolecular arrangements of Cp_2TaCl_2 showing lateral C-H···Cl interactions between those planes (right).

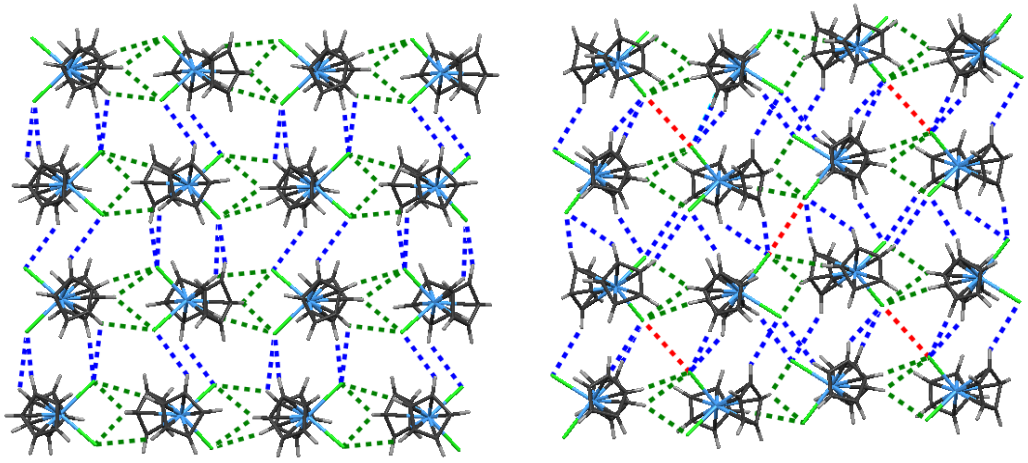

Figure S12 – Top views of secondary supramolecular arrangements between Cp_2TaCl_2 chains formed by type A (left) and type B molecules (right), involving C-H···Cl interactions (in blue) and Cl···Cl interactions (red).

Table S10 - Intermolecular contact parameters in Cp_2TaCl_2.

Chain interactions				
	C···Cl (Å)	H···Cl (Å)	C-H···Cl (°)	H···Cl-M (°)
C4-H4···Cl1	3.830	2.999	146.8	133.6
C4'-H4'···Cl1	3.717	2.901	144.7	90.1
C3-H3···Cl1'	3.815	2.873	171.4	119.6
C4'-H4'···Cl1'	3.760	2.933	146.1	89.7
C9-H9···Cl2	3.832	2.941	186.7	90.1
C9-H9···.Cl2'	3.797	3.058	135.8	87.5
C9'-H9'···Cl2'	3.907	2.964	172.2	115.9
Chain-chain interactions				
	C···Cl (Å)	H···Cl (Å)	C-H···Cl (°)	H···Cl-M (°)
C6-H6···Cl1'	3.699	3.102	122.4	96.1
C1'-H1'···Cl2	3.962	3.089	153.5	95.1
Plane-plane interactions				
	C···Cl (Å)	H···Cl (Å)	C-H···Cl (°)	H···Cl-M (°)
C2-H2···Cl1	3.693	2.956	135.3	94.9
C4-H4···Cl1'	3.980	3.322	128.2	138.0
C5'-H5'...Cl1'	3.779	2.920	151.0	118.6
C10-H10···Cl2	3.836	2.990	149.2	90.7
C8-H8···Cl2'	3.802	2.905	157.9	122.0
C8'-H8'···Cl2'	3.797	3.031	138.8	87.3
C-H···π interactions				
C3-H3···π_{II}	D_{pln} = 2.783 Å	D_{cp} = 2.041Å	α = 119.7º	
C1-H1···π_{II}	D_{pln} = 2.908 Å	D_{cp} = 1.581Å	α = 93.7°	
Halogen interactions				
Cl2'···Cl2' (Å)	Ta2-Cl2'···Cl2' (°)			
3.705	164.7			

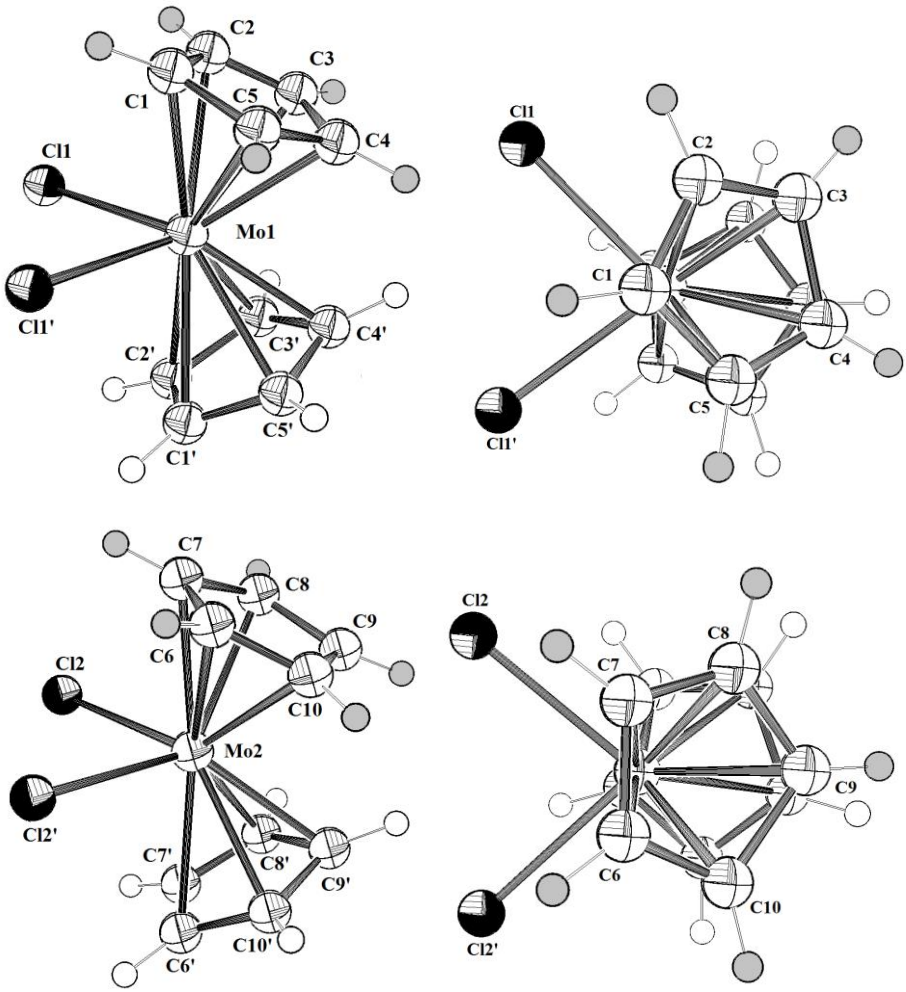

Figure S13. ORTEP diagram, drawn with 50% probability ellipsoids, showing the atomic labelling scheme for the two types of molecules of CPCLMO (Cp_2MoCl_2) (type A molecules on top, type B below).

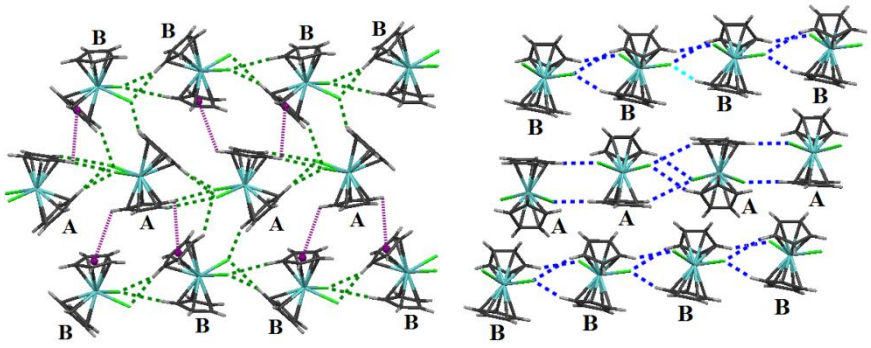

Figure S14 – Primary supramolecular arrangement of Cp_2MoCl_2: planes of chains formed by C-H···Cl interactions (in green) and C-H···π contacts (in purple) between Type I and Type II molecules (left). Front view of secondary supramolecular arrangements of Cp_2MoCl_2 showing lateral C-H···Cl interactions between those planes (right).

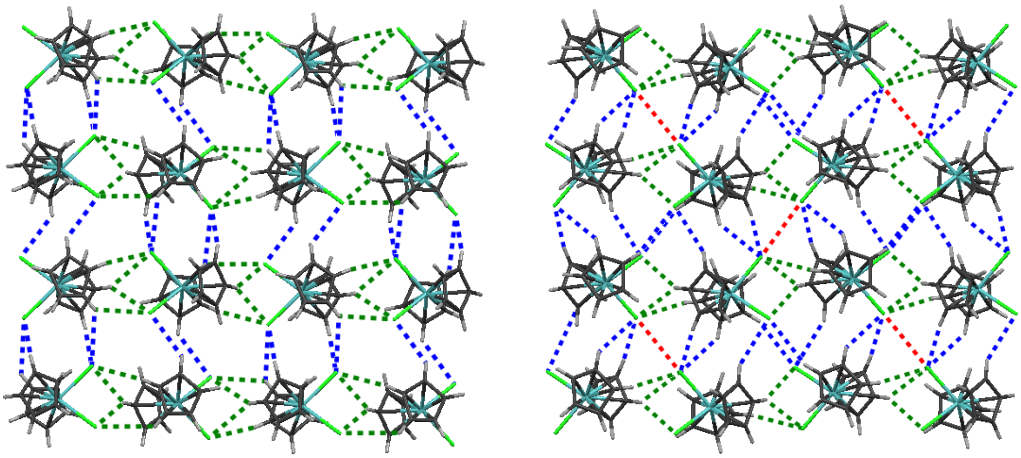

Figure S15 – Top views of secondary supramolecular arrangements between Cp_2MoCl_2 chains formed by type A (left) and type B molecules (right), involving C-H···Cl interactions (in blue) and Cl···Cl interactions (red).

Table S11 – Intermolecular contact parameters in Cp_2MoCl_2.

Chain interactions				
	C···Cl (Å)	H···Cl (Å)	C-H···Cl (°)	H···Cl-M (°)
C4-H4···Cl1	3.691	2.751	170.6	120.4
C4'-H4'···Cl1	3.642	2.835	143.3	89.5
C3-H3···Cl1'	3.804	3.125	129.8	141.8
C4'-H4'···Cl1'	3.568	2.753	144.4	91.6
C9'-H9'···Cl2	3.699	2.845	150.1	88.3
C9-H9···Cl2'	3.699	2.760	169.8	116.0
C9'-H9'···Cl2'	3.569	2.798	138.9	89.4
Chain-chain interactions				
	C···Cl (Å)	H···Cl (Å)	C-H···Cl (°)	H···Cl-M (°)
C6'-H6'···Cl1	3.663	3.082	121.0	84.5
C2'-H2'···Cl2	3.822	2.950	153.1	95.7
Plane-plane interactions				
	C···Cl (Å)	H···Cl (Å)	C-H···Cl (°)	H···Cl-M (°)
C3-H3···Cl1	3.837	3.095	136.2	132.6
C3'-H3'···Cl1	3.685	2.806	154.3	117.8
C5-H5···Cl1'	3.590	2.836	137.1	92.6
C10'-H10'···Cl2	3.782	2.949	147.1	89.0
C8-H8···Cl2'	3.674	2.874	142.6	87.2
C8'-H8'···Cl2'	3.708	2.800	160.1	123.5
C-H···π interactions				
C4-H4···π_{II}	D_{pln} = 2.672 Å	D_{cp} = 1.690 Å	α = 91.7º	
C1-H1···π_{II}	D_{pln} = 2.873 Å	D_{cp} = 2.021 Å	α = 121.5°	
Halogen interactions				
Cl2'···Cl2' (Å)	Ta1-Cl2'···Cl2' (°)			
3.693	164.3			

Table S12 – Intermolecular contact parameters in Cp_2TiBr_2.

Chain interactions				
	C···Br (Å)	H···Br (Å)	C-H···Br (°)	H···Br-M (°)
C8-H8···Br1	3.859	3.118	136.1	120.0
C8'-H8'···Br1	3.870	2.934	171.1	101.6
C9-H9···Br1'	3.815	2.872	171.9	100.0
C9'-H9'···Br1'	3.736	3.113	124.7	136.8
C3-H3···Br2	3.989	3.047	171.3	105.4
C3'-H3'···Br2	3.831	3.047	140.5	120.7
C4-H4···Br2'	3.927	3.264	128.6	134.6
C4'-H4'···.Br2'	3.880	2.946	169.0	104.5
Plane-plane interactions				
	C···Br (Å)	H···Br (Å)	C-H···Br (°)	H···Br-M (°)
C3-H3···Br1	3.909	3.151	137.7	137.9
C2'-H2'···Br1	3.630	3.242	133.6	107.2
C10-H10··· Br1'	3.776	3.006	139.2	115.1
C9'-H9'···Br1'	4.132	3.317	145.1	111.8
C8-H8···Br2	3.875	3.085	141.6	136.6
C7'-H7'···Br2	3.941	3.194	136.7	107.9
C5-H5···Br2'	3.916	3.247	129.0	113.1
C4'-H4'···Br2'	3.925	3.106	145.4	119.6
C-H···π interactions				
C10'-H10'···π_I	D_{pln} = 2.858 Å	D_{cp} = 3.224 Å	α = 114.7°	
C7-H7···π_{II}	D_{pln} = 2.859 Å	D_{cp} = 2,869 Å	α = 117.7º	
Halogen interactions				
Br1···Br2 (Å)	Ti1-Br1…Br2 (º)	Ti2-Br2…Br1 (º)		
3.999	168.8	170.6		

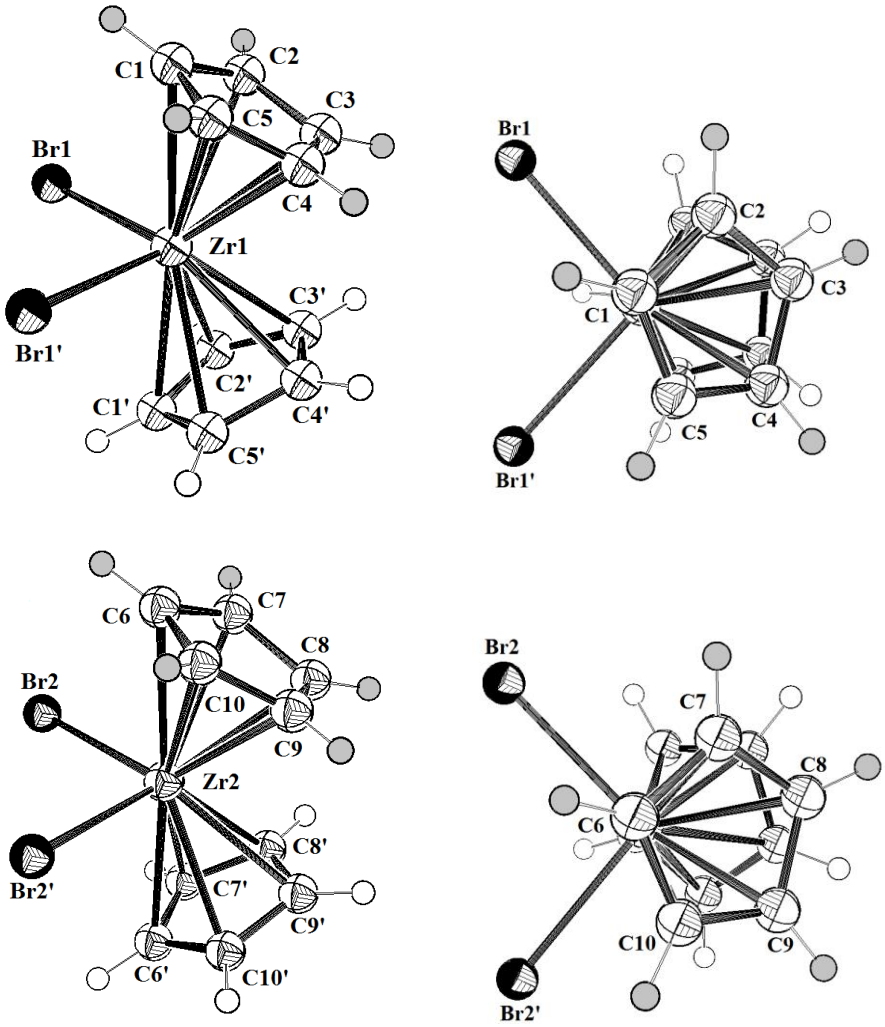

Figure S16. ORTEP diagram, drawn with 50% probability ellipsoids, showing the atomic labelling scheme for the two types of molecules of ZUJLOF (Cp_2ZrBr_2) (type A molecules on top, type B below).

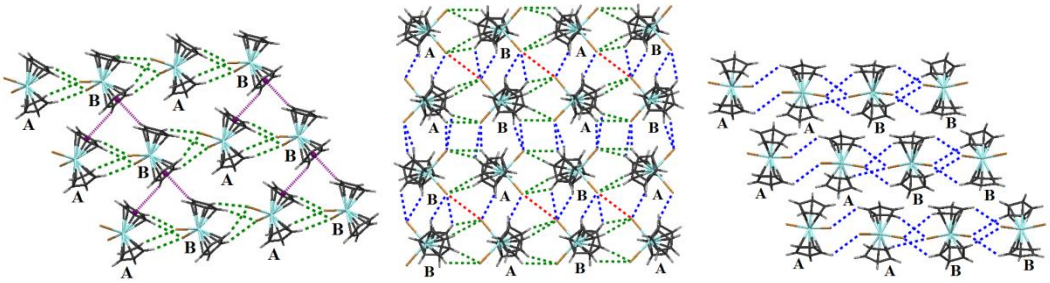

Figure S17 – Supramolecular arrangement of Cp_2ZrBr_2. Planes of chains formed by C-H···Br interactions (in green) and C-H···π contacts (in purple) (left). Interaction between these planes by C-H···Br interactions (in blue) and Br···Br interactions (in red): top (centre) and front (right) views.

Table S13 – Intermolecular contact parameters in Cp_2ZrBr_2.

Chain interactions				
	C···Br (Å)	H···Br (Å)	C-H···Br (°)	H···Br-M (°)
C8-H8···Br1	3.908	2.968	166.5	99.0
C8'-H8'···Br1	3.957	3.194	137.8	115.4
C9-H9···Br1'	3.808	3.144	127.7	132.6
C9'-H9'···Br1'	3.909	2.980	163.3	95.7
C3-H3···Br2	3.753	2.823	165.0	108.0
C3'-H3'···Br2	4.067	3.133	164.8	102.3
C4-H4···Br2'	3.967	3.127	148.3	108.0
C4'-H4'···.Br2'	3.995	3.294	131.4	131.0
Plane-plane interactions				
	C···Br (Å)	H···Br (Å)	C-H···Br (°)	H···Br-M (°)
C2'-H2'···Br1	3.970	3.346	124.6	108.0
C10'-H10'··· Br1'	3.838	3.123	132.7	116.9
C9-H9···Br1'	4.196	3.448	136.4	114.4
C8'-H8'···Br2	3.954	3.229	133.8	134.5
C7-H7···Br2	3.985	3.316	128.5	108.9
C4-H4···Br2'	3.882	3.254	125.3	148.0
C4'-H4'···Br2'	3.998	3.243	136.9	118.9
C-H···π interactions				
C10-H10···π_I	D_{pln} = 2.132 Å	D_{cp} = 0.706 Å	α = 145.5°	
C7'-H7'···π_{II}	D_{pln} = 2.922 Å	D_{cp} = 0.488 Å	α = 117.2°	
Halogen interactions				
Br1···Br2 (Å)	Zr1-Br1…Br2 (°)	Zr2-Br2…Br1 (°)		
3.916	166.6	168.1		

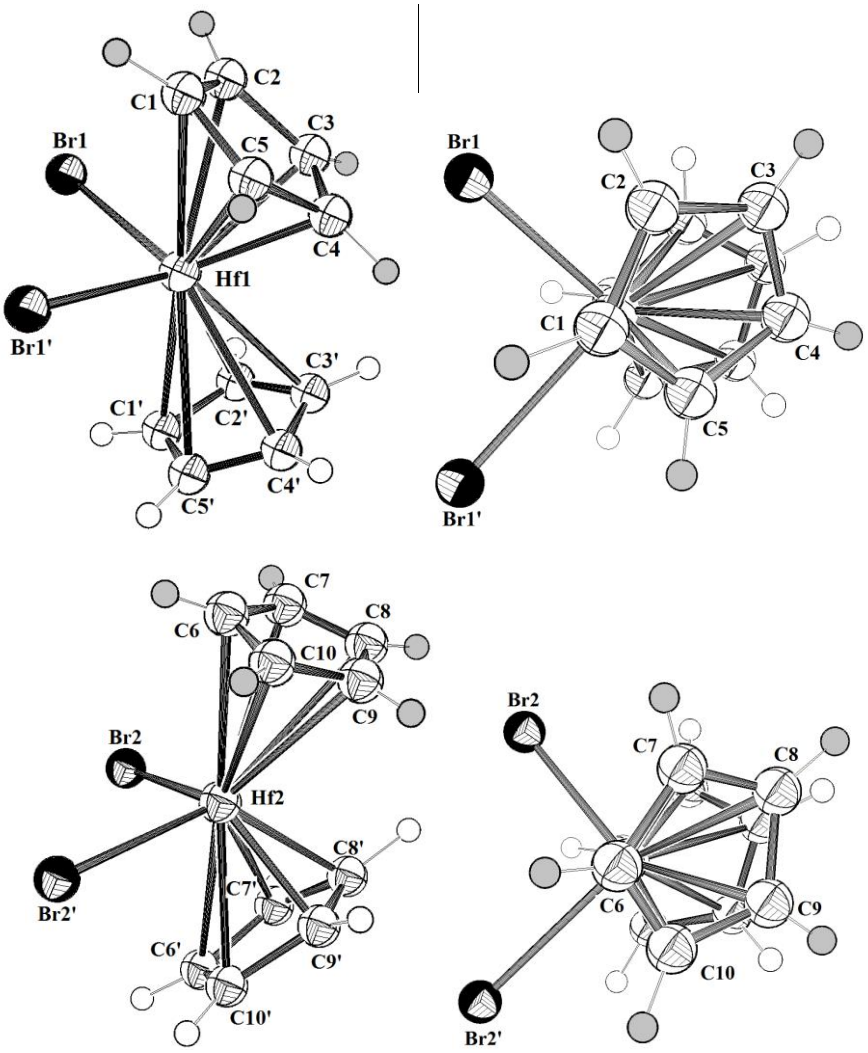

Figure S18. ORTEP diagram, drawn with 50% probability ellipsoids, showing the atomic labelling scheme for the two types of molecules of VIVMES (Cp_2HfBr_2) (type A molecules on top, type B below).

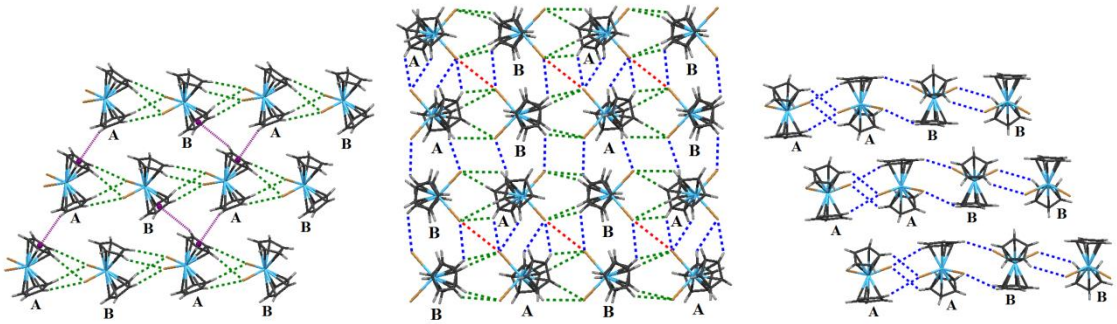

Figure S19 – Supramolecular arrangement of Cp_2HfBr_2. Planes of chains formed by C-H···Br interactions (in green) and C-H···π contacts (in purple) (left). Interaction between these planes by C-H···Br interactions (in blue) and Br···Br interactions (in red): top (centre) and front (right) views.

Table S14 – Intermolecular contact parameters in Cp_2HfBr_2.

Chain interactions				
	C···Br (Å)	H···Br (Å)	C-H···Br (°)	H···Br-M (°)
C8-H8···Br1	4.089	3.135	174.1	108.2
C8'-H8'···Br1	3.893	3.026	151.8	114.6
C9-H9···Br1'	4.007	3.243	138.6	128.8
C9'-H9'···Br1'	4.002	3.095	159.8	107.0
C3-H3···Br2	3.983	3.249	135.1	118.2
C3'-H3'···Br2	3.981	3.033	176.6	103.5
C4-H4···Br2'	3.899	2.957	175.0	99.5
C4'-H4'···.Br2'	3.897	3.220	130.5	132.5
Plane-plane interactions				
	C···Br (Å)	H···Br (Å)	C-H···Br (°)	H···Br-M (°)
C3-H3···Br1	3.997	3.172	145.6	133.2
C2'-H2'···Br1	4.001	3.294	132.4	106.4
C9'-H9'···Br1'	4.073	3.297	140.0	122.9
C8-H8···Br2	4.039	3.351	130.8	139.2
C5-H5···Br2'	3.872	3.135	136.1	114.7
C-H···π interactions				
C10-H10···π_I	D_{pln} = 2.935 Å	D_{cp} = 1.122 Å	α = 116.0°	
C2-H2···π_{II}	D_{pln} = 2.863 Å	D_{cp} = 1.905 Å	α = 115.3º	
Halogen interactions				
Br1···Br2 (Å)	Hf1-Br1…Br2 (º)	Hf2-Br2…Br1 (º)		
3.967	169.5	168.3		

Table S15 – Intermolecular contact parameters in Cp_2TiI_2.

Chain interactions				
	C···I(Å)	H···I (Å)	C-H···I (°)	H···I-M (°)
C3-H3···I	4.138	3.362	136.8	123.0
C3'-H3'···I	4.032	3.018	168.2	110.7
C4-H4···I'	4.032	3.018	168.2	110.7
C4'-H4'···I'	4.138	3.362	136.8	123.0
Plane-plane interactions				
	C···I (Å)	H···I (Å)	C-H···I (°)	H···I-M (°)
C3-H3···I	4.075	3.251	142.1	133.4
C4'-H4'···I'	4.075	3.251	142.1	133.4
C-H···π interactions				
C2-H2···π	D_{pln} = 2.769 Å	D_{cp} = 3.363 Å	α = 109.3°	
C5'-H5'···π	D_{pln} = 2.769 Å	D_{cp} = 3,363 Å	α = 109.3º	
Halogen interactions				
I1···I1 (Å)	T11-1l-I1 (°)			
4.108	171.6			

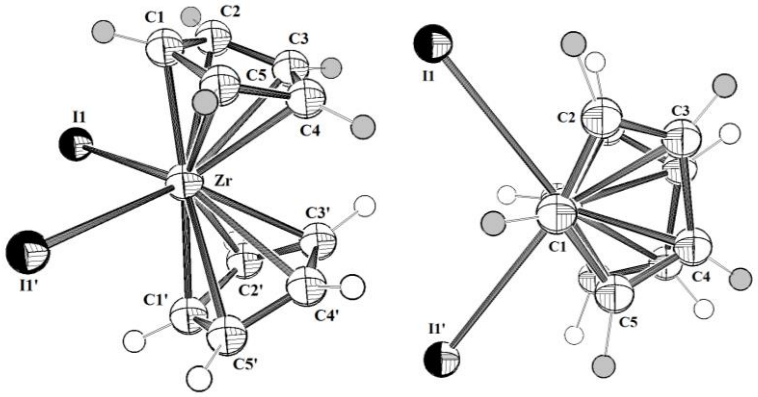

Figure S20. ORTEP diagram, drawn with 50% probability ellipsoids, showing the atomic labelling scheme for IDCPZR (Cp_2ZrI_2).

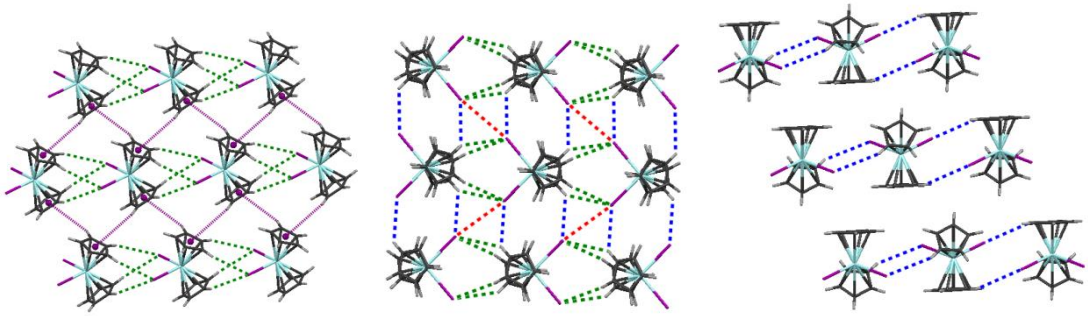

Figure S21 – Supramolecular arrangement of Cp_2ZrI_2. Planes of chains formed by C-H···I interactions (in green) and C-H···π contacts (in purple) (left). Interaction between these planes by C-H···I interactions (in blue) and I···I interactions (in red): top (centre) and front (right) views.

Table S16 – Intermolecular contact parameters in Cp_2ZrI_2.

Chain interactions				
	C···I(Å)	H···I (Å)	C-H···I (°)	H···I-M (°)
C3-H3···I	4.262	3.444	145.7	117.9
C3'-H3'···I	4.156	3.217	170.0	109.0
C4-H4···I'	4.156	3.214	171.4	108.5
C4'-H4'···I'	4.262	3.437	146.5	117.8
Plane-plane interactions				
	C···I (Å)	H···I (Å)	C-H···I (°)	H···I-M (°)
C3-H3···I	4.206	3.450	138.1	135.2
C4'-H4'···I'	4.205	3.455	137.5	135.4
C-H···π interactions				
C2-H2···π	D_{pln} = 2.969 Å	D_{cp} = 2.161 Å	α = 111.2°	
C5'-H5'···π	D_{pln} = 3.013 Å	D_{cp} = 2.166 Å	α = 108.3º	
Halogen interactions				
I1···I1 (Å)	Zr1-1l·I1 (°)			
4.123	170.1			

Table S17 – Intermolecular contact parameters in Cp_2MoH_2.

Chain interactions				
	C···H⁻(Å)	H···H⁻ (Å)	C-H···H⁻ (°)	H···H⁻-M (°)
C1-H1···H6	3.470	2.473	152.3	111.2
C1-H1···H6’	3.481	2.501	149.8	110.0
C1’-H1’···H6	3.481	2.501	149.8	110.0
C1’-H1’···H6’	3.470	2.473	152.3	111.2
Plane-plane interactions				
	C···H⁻(Å)	H···H⁻ (Å)	C-H···H⁻ (°)	H···H⁻-M (°)
C5-H5···H6	3.056	2.405	117.8	105.9
C2’-H2’···H6’	3.056	2.405	117.8	105.9
C-H···π interactions				
C3-H3···π	D_{pln} = 3.022 Å	D_{cp} = 0.130 Å	α = 117.1°	
C4’-H4’···π	D_{pln} = 3.022 Å	D_{cp} = 0.130 Å	α = 117.1°	

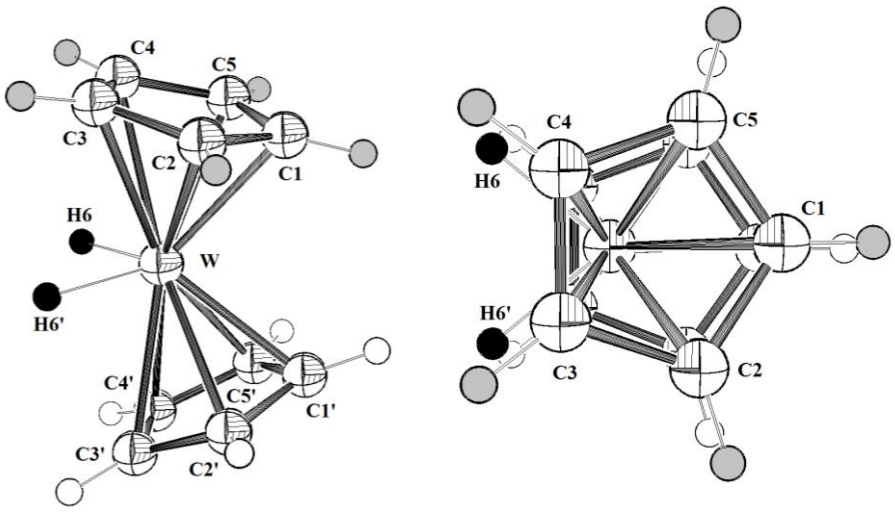

Figure S22. ORTEP diagram, drawn with 50% probability ellipsoids, showing the atomic labelling scheme for IDCPZR (Cp_2WH_2).

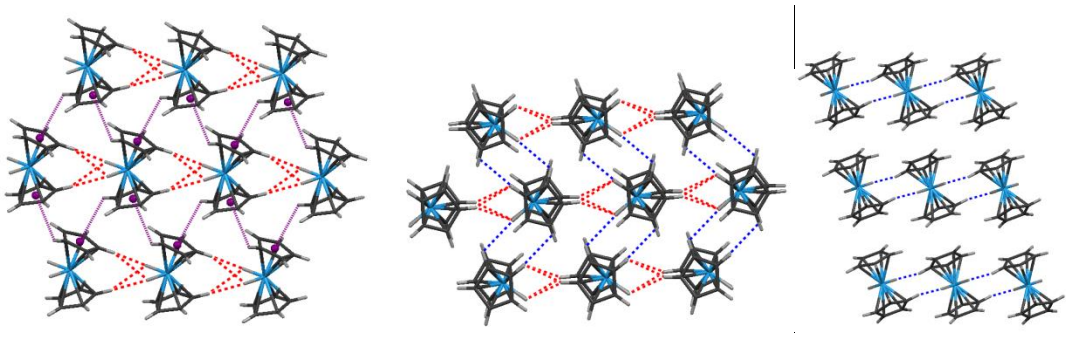

Figure S23 – Supramolecular arrangement of Cp_2WH_2. Planes of chains formed by C-H···H$^-$ interactions (in red) and C-H···π contacts (in purple) (left). Interaction between these planes by C-H···H$^-$ interactions (in blue): top (centre) and front (right) views.

Table S18 – Intermolecular contact parameters in Cp_2WH_2.

Chain interactions				
	C···H$^-$(Å)	H···H$^-$ (Å)	C-H···H$^-$ (°)	H···H$^-$-M (°)
C1-H1···H6	3.488	2.602	155.2	113.0
C1-H1···H6’	3.529	2.655	153.1	110,5
C1’-H1’···H6	3.529	2.655	153.1	110.5
C1’-H1’···H6’	3.488	2.602	155.21	113.0
Plane-plane interactions				
	C···H$^-$(Å)	H···H$^-$ (Å)	C-H···H$^-$ (°)	H···H$^-$-M (°)
C5-H5···H6	3.089	2.536	117.3	175.2
C2’-H2’···H6’	3.089	2.536	117.3	175.2
C-H···π interactions				
C3-H3···π	D_{pln} = 3.006 Å	D_{cp} = 0.528 Å	α = 119.1°	
C4’-H4’···π	D_{pln} = 3.006 Å	D_{cp} = 0.528 Å	α = 119.1°	