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Supporting information for article:

Similarities and differences in the crystal packing of halogen substituted Indole derivatives

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Table S1: Weights and corresponding yields of product for **Hx**

Entry	Substitution	Sample code	Phenylhydrazine (g)	Cyclohexanone (ml)	Product (g)	Yield (%)
1	Unsubstituted	HxP	0.186	0.178	0.280	94
2	*o*- F	HxF_2	0.3	0.250	0.410	91
3	*m*-F	HxF_3	0.5	0.410	0.657	88
4	*p*- F	HxF_4	0.5	0.410	0.670	89
5	*o*-Cl	$HxCl_2$	0.5	0.218	0.690	96
6	*m*-Cl	$HxCl_3$	0.5	0.363	0.673	93.5
7	*p*-Cl	$HxCl_4$	0.5	0.363	0.685	95
8	*o*-Br	$HxBr_2$	0.5	0.280	0.628	94
9	*m*-Br	$HxBr_3$	0.5	0.280	0.590	88
10	*p*-Br	$HxBr_4$	0.5	0.280	0.610	91

Table S2: Weights and corresponding yields of product for **Hp**

Entry	Substitution	Sample code	Phenylhydrazine (g)	Cycloheptanone (ml)	Product(g)	Yield (%)
1	Unsubstituted	HpP	0.186g	0.178ml	0.280g	94
2	*o*- F	HpF_2	0.3	0.281	0.455	95
3	*m*-F	HpF_3	0.3	0.281	0.421	88
4	*p*- F	HpF_4	0.3	0.281	0.433	91
5	*o*-Cl	$HpCl_2$	0.5	0.415	0.745	97
6	*m*-Cl	$HpCl_3$	0.5	0.415	0.690	80
7	*p*-Cl	$HpCl_4$	0.5	0.415	0.730	95
8	*o*-Br	$HpBr_2$	0.5	0.280	0.690	98
9	*m*-Br	$HpBr_3$	0.5	0.280	0.65	92
10	*p*-Br	$HpBr_4$	0.5	0.280	0.678	96

Table S3: List of chemical shift (δ in ppm) for N-H and IR stretching frequency (in cm^{-1}) of N-H bond

S.N.	Sample Code	FTIR(N-H)	N-H (δ)	S.N.	Sample Code	FTIR (N-H)	N-H (δ)
1	HxP	3393	7.57	**11**	HpP	3422	7.82
2	HxF2	3395	7.76	**12**	HpF2	3398	7.85
3	HxF3	3395	7.59	**13**	HpF3	3402	7.79
4	HxF4	3408	7.59	**14**	HpF4	3399	7.76
5	HxCl2	3421	7.76	**15**	HpCl2	3392	7.81
6	HxCl3	3395	7.66	**16**	HpCl3	3399	7.58

7	HxCl4	3405	7.66	**17**	HpCl4	3402	7.58
8	HxBr2	3340	7.62	**18**	HpBr2	3395	7.54
9	HxBr3	3407	7.59	**19**	HpBr3	3400	7.63
10	HxBr4	3406	7.62	**20**	HpBr4	3404	7.63

For Series Hx

1. 2,3,4,9-tetrahydro-1H-carbazole (HxP): Yield**:** 94%, FTIR (in cm^{-1}: KBr): 3393, 2925, 1623, ^{1}H NMR (400 MHz, $CDCl_3$)) δ 7. 59 (s, 1H), 7.41 (d, 1H), 7.05 (dd, *J* = 8.5, 5.4 Hz, 1H), 6.80 (dd, *J* = 9.8, 2.2 Hz, 1H), 6.77 – 6.72 (m, 1H), 2.65 – 2.58 (m, *J* = 5.9 Hz, 2H), 2.59 (t, *J* = 5.9 Hz, 2H) 1.81 (tt, *J* = 10.4, 5.0 Hz, 4H).

2. 8-fluoro-2,3,4,9-tetrahydro-1H-carbazole (HxF2): Yield**:** 91%, FTIR (in cm^{-1}: KBr): 3395, 2926, 1625, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 6.89 (td, *J* = 7.9, 4.8 Hz, 1H), 6.75 (dd, *J* = 11.2, 7.9 Hz, 1H), 2.68 (t, *J* = 5.9 Hz, 2H), 2.63 (t, *J* = 5.9 Hz, 2H), 1.88 – 1.76 (m, 4H).

3. 7-fluoro-2,3,4,9-tetrahydro-1H-carbazole(HxF3): Yield**:** 88%, FTIR (in cm^{-1}: KBr): 3395, 2926, 1625, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.27 (dd, *J* = 8.5, 5.4 Hz, 1H), 6.89 (dd, *J* = 9.8, 2.2 Hz, 1H), 6.79 – 6.72 (m, 1H), 2.67 – 2.58 (m, *J* = 5.9 Hz, 2H), 2.61 (t, *J* = 5.9 Hz, 2H) 1.81 (tt, *J* = 10.4, 5.0 Hz, 4H).

4. 6-fluoro-2,3,4,9-tetrahydro-1H-carbazole (HxF4): Yield**:** 89%, FTIR (in cm^{-1}: KBr): 3408, 2933, 1583, 1446, ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (s, 1H), 7.10 (dd, *J* = 8.7, 4.3 Hz, 1H), 7.02 (dd, *J* = 9.6, 2.4 Hz, 1H), 6.77 (t, *J* = 9.1 Hz, 1H), 2.65 (t, *J* = 5.7 Hz, 2H), 2.59 (t, *J* = 5.7 Hz, 2H), 1.90 – 1.74 (m, 4H).

5. 8-chloro-2,3,4,9-tetrahydro-1H-carbazole(HxCl2): Yield**:** 96%, FTIR (in cm^{-1}: KBr): 3421, 2931, 1673, 1466, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 6.89 (td, *J* = 7.9, 4.8 Hz, 1H), 6.75 (dd, *J* = 11.2, 7.9 Hz, 1H), 2.68 (t, *J* = 5.9 Hz, 2H), 2.63 (t, *J* = 5.9 Hz, 2H), 1.88 – 1.76 (m, 4H).

6. 7-chloro-2,3,4,9-tetrahydro-1H-carbazole(HxCl3): Yield**:** 93.5%, FTIR (in cm^{-1}: KBr): 3395, 2935, 1645, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.54 (m, 1H), 7.36 – 7.31 (m, 1H), 7.11 – 7.06 (m, 1H), 7.00 – 6.95 (m, 1H), 2.64 (t, *J* = 5.8 Hz, 2H), 2.58 (t, *J* = 5.8 Hz, 2H), 1.88 – 1.74 (m, 4H).

7. 6-chloro-2,3,4,9-tetrahydro-1H-carbazole(HxCl4): Yield**:** 95%, FTIR (in cm^{-1}: KBr): 3405, 2937, 1654, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.54 (m, 1H), 7.36 – 7.31 (m, 1H), 7.11 – 7.06 (m, 1H), 7.00 – 6.95 (m, 1H), 2.64 (t, *J* = 5.8 Hz, 2H), 2.58 (t, *J* = 5.8 Hz, 2H), 1.88 – 1.74 (m, 4H).

8. 8-bromo-2,3,4,9-tetrahydro-1H-carbazole (HxBr2): Yield**:** 94%, FTIR (in cm^{-1}: KBr): 3340, 2930, 1670, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.49 (d, *J* = 1.2 Hz, 1H), 7.11 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 2.65 (t, *J* = 5.9 Hz, 2H), 2.58 (t, *J* = 5.8 Hz, 2H), 1.87 – 1.75 (m, 4H).

9. 7-bromo-2,3,4,9-tetrahydro-1H-carbazole(HxBr3): Yield**:** 88%, FTIR (in cm^{-1}: KBr): 3407, 2932, 1640, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.31 (d, *J* = 1.5 Hz, 1H), 7.24 (d, *J* = 8.4 Hz, 1H), 7.09 (dd, *J* = 8.4, 1.6 Hz, 1H), 2.77 – 2.66 (m, 5H), 1.69 (d, *J* = 8.3 Hz, 5H).

10. 6-bromo-2,3,4,9-tetrahydro-1H-carbazole(HxBr4): Yield**:** 91%, FTIR (in cm^{-1}: KBr): 3406, 2901, 1627, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.49 (d, *J* = 1.2 Hz, 1H), 7.11 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 2.65 (t, *J* = 5.9 Hz, 2H), 2.58 (t, *J* = 5.8 Hz, 2H), 1.87 – 1.75 (m, 4H).

For Series Hp

1. 5,6,7,8,9,10-hexahydrocyclohepta[b]indole (HpP): Yield**:** 94%, FTIR (in cm^{-1}: KBr): 3422, 1647, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.19 (d, j=8.0 Hz,1H), 7.13 (d, *J* = 8.0 Hz, 1H), 6.85 (td, *J* = 7.9, 4.8 Hz, 1H), 6.78 (dd, *J* = 11.1, 7.8 Hz, 1H), 2.89 – 2.73 (m, 4H), 1.88 (dd, *J* = 10.2, 5.4 Hz, 2H), 1.82 – 1.72 (m, 4H) .

2. 4-fluoro-5,6,7,8,9,10-hexahydrocyclohepta[b]indole(HpF2): Yield**:** 95%, FTIR (in cm^{-1}: KBr): 3398, 2914, 1582, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 6.95 (td, *J* = 7.9, 4.8 Hz, 1H), 6.78 (dd, *J* = 11.1, 7.8 Hz, 1H), 2.89 – 2.73 (m, 4H), 1.88 (dd, *J* = 10.2, 5.4 Hz, 2H), 1.82 – 1.72 (m, 4H) .

3. 3-fluoro-5,6,7,8,9,10-hexahydrocyclohepta[b]indole(HpF3): Yield**:** 88%, FTIR (in cm^{-1}: KBr): 3402, 2917,1445, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 6.90 (td, *J* = 7.9, 4.8 Hz, 1H), 6.75 (dd, *J* = 11.2, 7.9 Hz, 1H), 2.68 (t, *J* = 5.9 Hz, 4H), 2.63 (t, *J* = 5.9 Hz, 2H), 1.90 – 1.76 (m, 4H).

4. 2-fluoro-5,6,7,8,9,10-hexahydrocyclohepta[b]indole(HpF4): Yield**:** 91%, FTIR (in cm^{-1}: KBr): 3391, 2919, 1578, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.14 (d, *J* = 7.8 Hz, 1H), 6.90 (td, *J* = 7.9, 4.8 Hz, 1H), 6.75 (dd, *J* = 11.2, 7.9 Hz, 1H), 2.68 (t, *J* = 5.9 Hz, 4H), 2.63 (t, *J* = 5.9 Hz, 2H), 1.90 – 1.76 (m, 4H).

5. 4-chloro-5,6,7,8,9,10-hexahydrocyclohepta[b]indole(HpCl2): Yield**:** 97%, FTIR (in cm^{-1}: KBr): 3393, 2925, 1624, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.7 Hz, 1H), 2.82 – 2.76 (m, 2H), 2.75 – 2.68 (m, 2H), 1.81 (dd, *J* = 7.3, 3.3 Hz, 2H), 1.70 (dt, *J* = 10.4, 5.2 Hz, 4H).

6. 3-chloro-5,6,7,8,9,10-hexahydrocyclohepta[b]indole(HpCl3): Yield**:** 80%, FTIR (in cm^{-1}: KBr): 3399, 1641, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.15 (d, *J* = 1.6 Hz, 1H), 6.96 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.78 – 2.66 (m, 4H), 1.86 – 1.77 (m, 2H), 1.75 – 1.64 (m, 4H).

7. 2-chloro-5,6,7,8,9,10-hexahydrocyclohepta[b]indole(HpCl4): Yield**:** 95%, FTIR (in cm^{-1}: KBr): 3402, 2928,1634, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 7.15 (d, *J* = 1.6 Hz, 1H), 6.96 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.78 – 2.66 (m, 4H), 1.86 – 1.77 (m, 2H), 1.75 – 1.64 (m, 4H).

8. 4-bromo-5,6,7,8,9,10-hexahydrocyclohepta[b]indole(HpBr2): Yield**:** 98%, FTIR (in cm^{-1}: KBr): 3396, 2919, 1623, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.13 (dd, *J* = 17.3, 9.7 Hz, 1H), 7.08 (dd, *J* = 8.4, 1.6 Hz, 1H), 2.73 – 2.67 (m, 4H), 1.83 – 1.78 (m, 2H), 1.70 – 1.66 (m, 4H).

9. 3-bromo-5,6,7,8,9,10-hexahydrocyclohepta[b]indole(HpBr3): Yield**:** 92%, FTIR (in cm^{-1}: KBr): 3401, 2919, 1636, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.51 (d, *J* = 1.3 Hz, 1H), 7.08 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 2.78 – 2.72 (m, 2H), 2.70 – 2.65 (m, 2H), 1.85 – 1.78 (m, 2H), 1.73 – 1.64 (m, 4H).

10. 2-bromo-5,6,7,8,9,10-hexahydrocyclohepta[b]indole(HpBr4): Yield**:** 96%, FTIR (in cm^{-1}: KBr): 3405, 2919, 1638, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.51 (d, *J* = 1.3 Hz, 1H), 7.08 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.04 (d, *J* = 8.5 Hz, 1H), 2.78 – 2.72 (m, 2H), 2.70 – 2.65 (m, 2H), 1.85 – 1.78 (m, 2H), 1.73 – 1.64 (m, 4H).

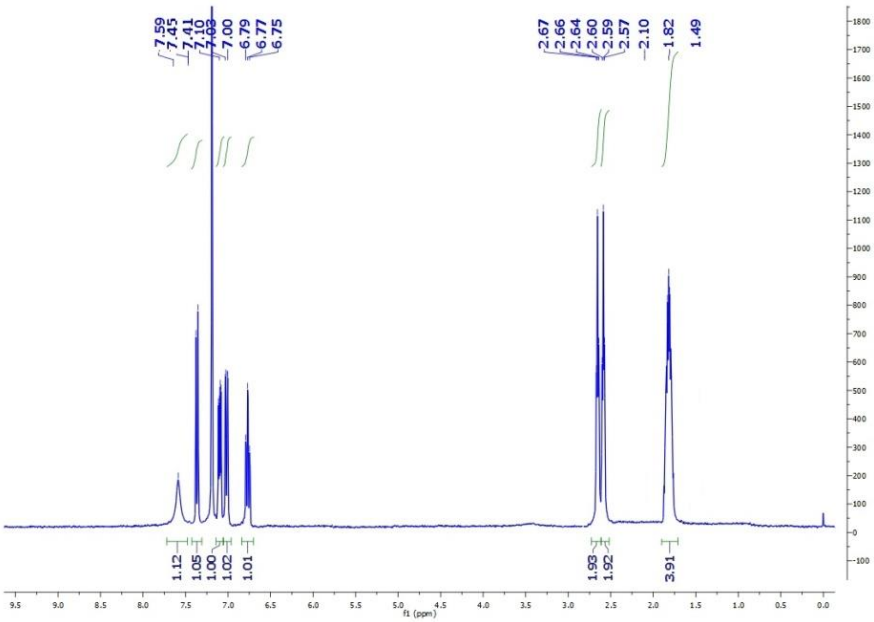

Figure S1a: ^{1}HNMR spectra of HxP in $CDCl_3$

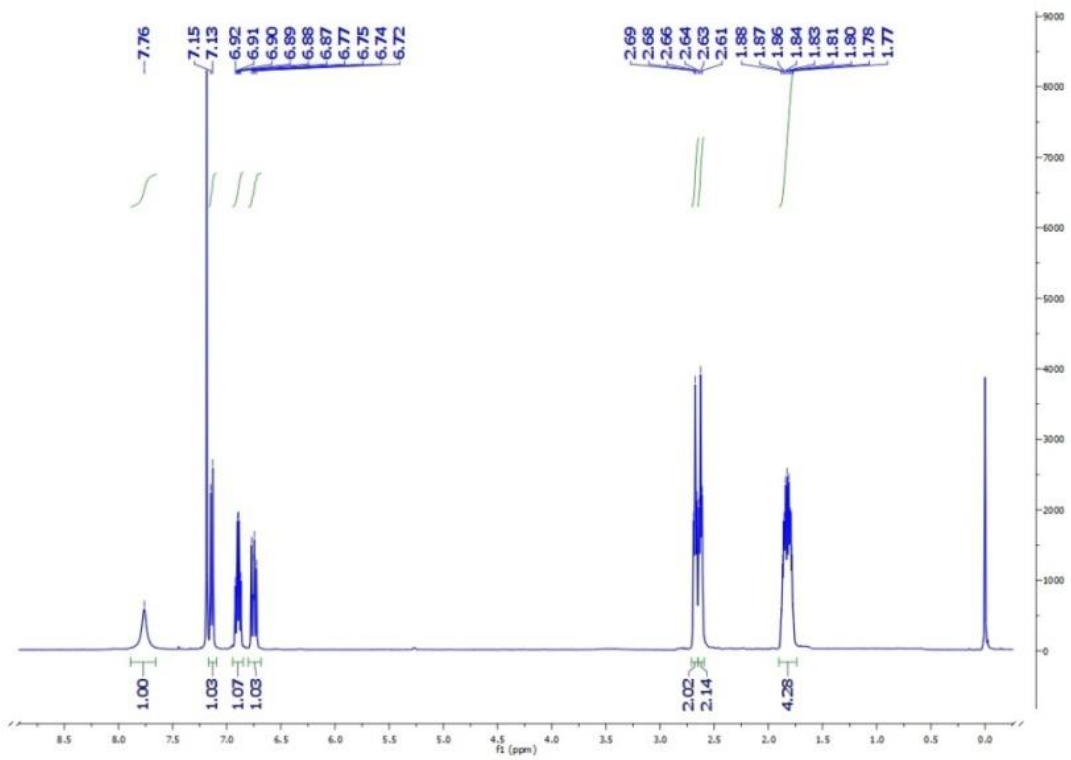

Figure S1b: ^{1}HNMR spectra of HxF2in $CDCl_3$

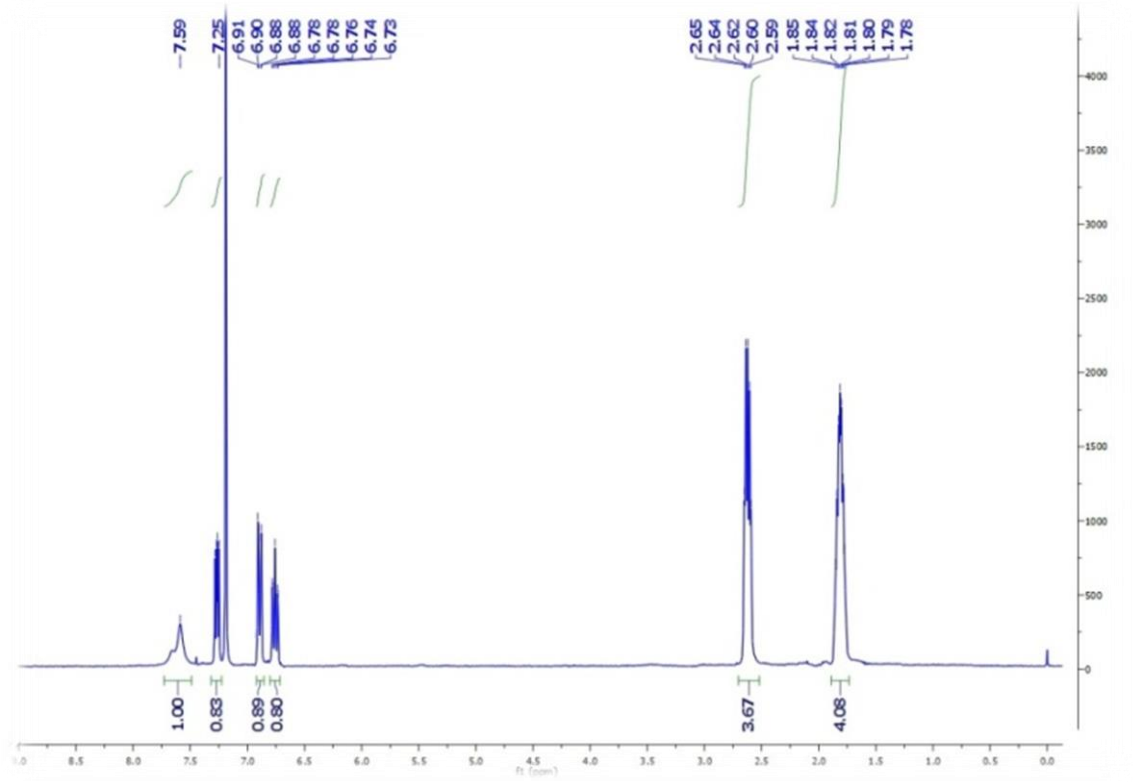

Figure S1c: ^{1}HNMR spectra of HxF3in $CDCl_3$

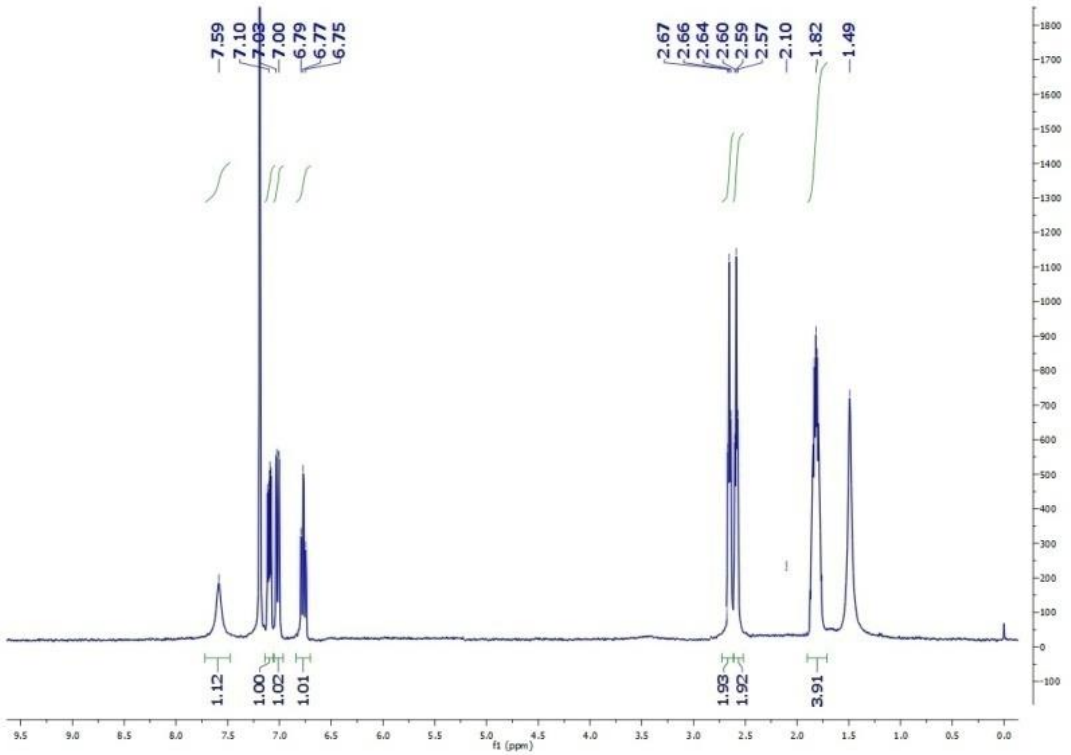

Figure S1d: ^{1}HNMR spectra of HxF4in $CDCl_3$

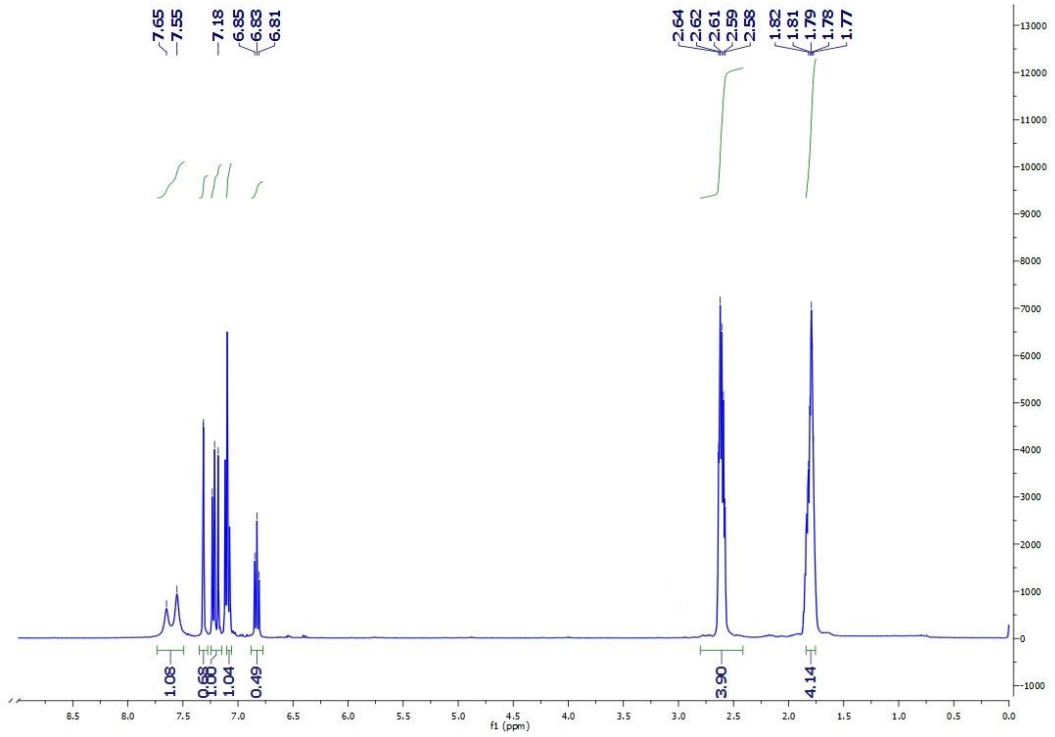

Figure S1e: ^{1}HNMR spectra of HxCl2in $CDCl_3$

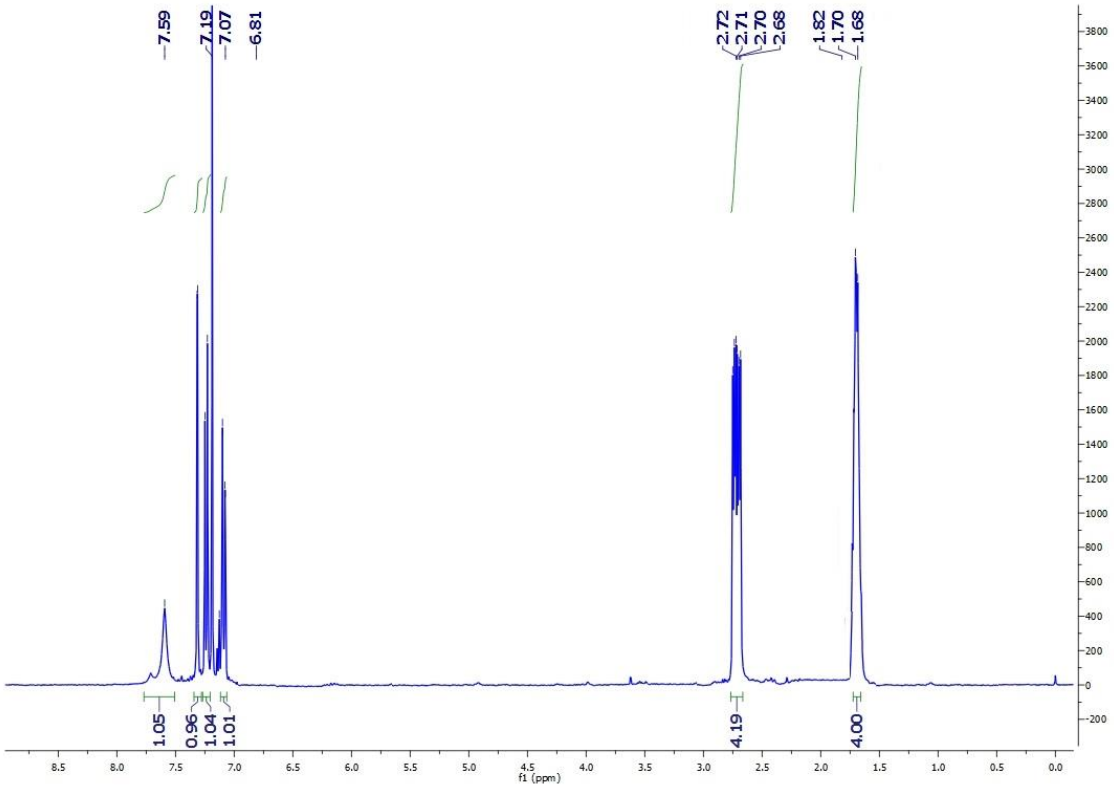

Figure S1f: ^{1}HNMR spectra of HxCl3 in $CDCl_3$

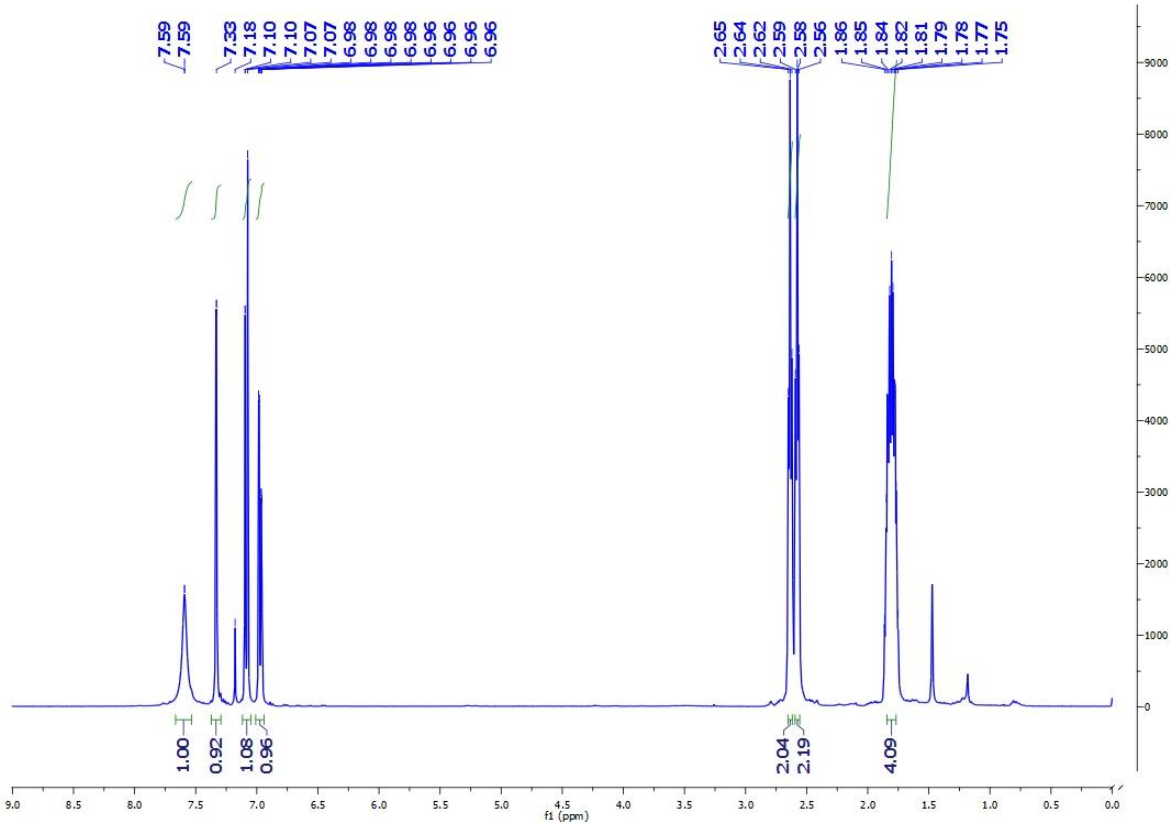

Figure S1g: ^{1}HNMR spectra of HxCl4 in $CDCl_3$

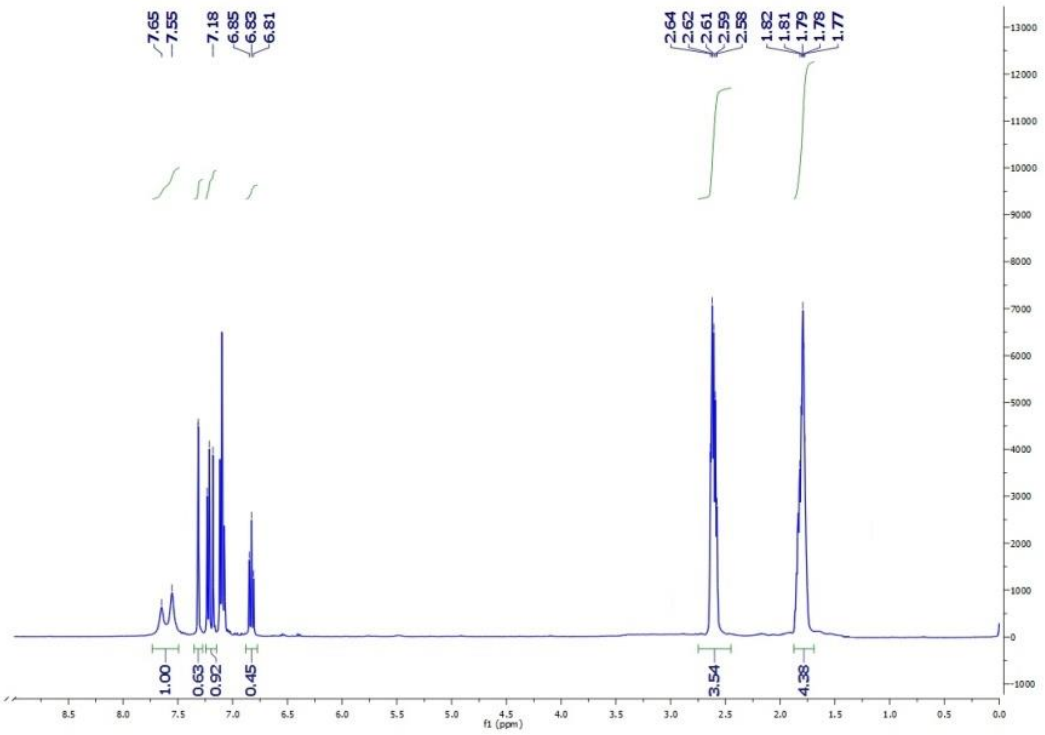

Figure S1h: ^{1}HNMR spectra of HxBr2 in $CDCl_3$

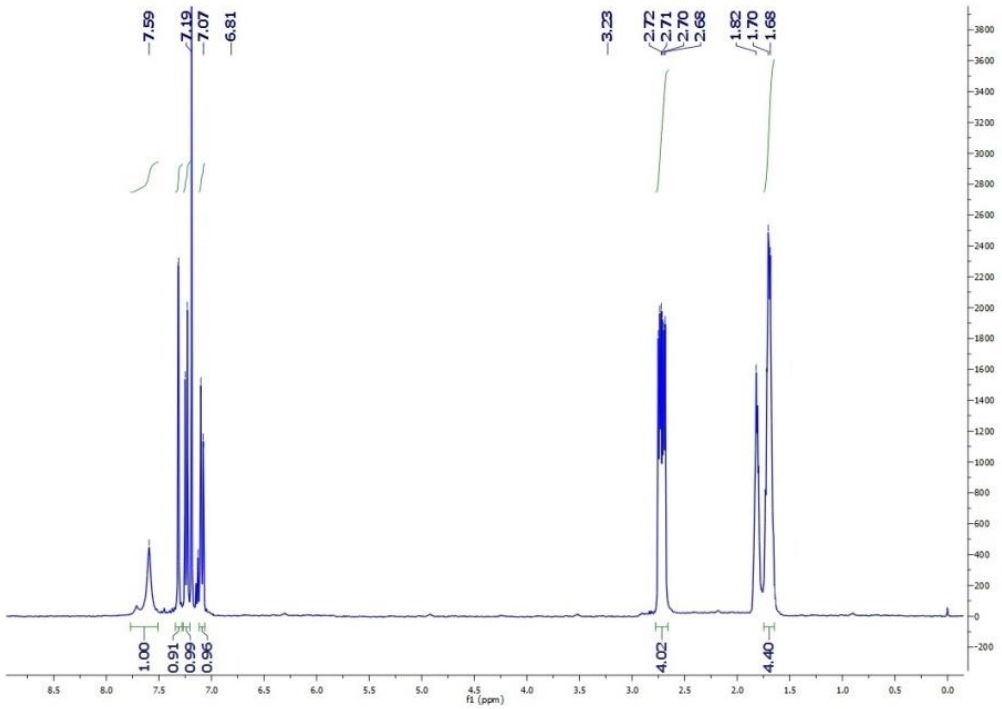

Figure S1i: ^{1}HNMR spectra of HxBr3 in $CDCl_3$

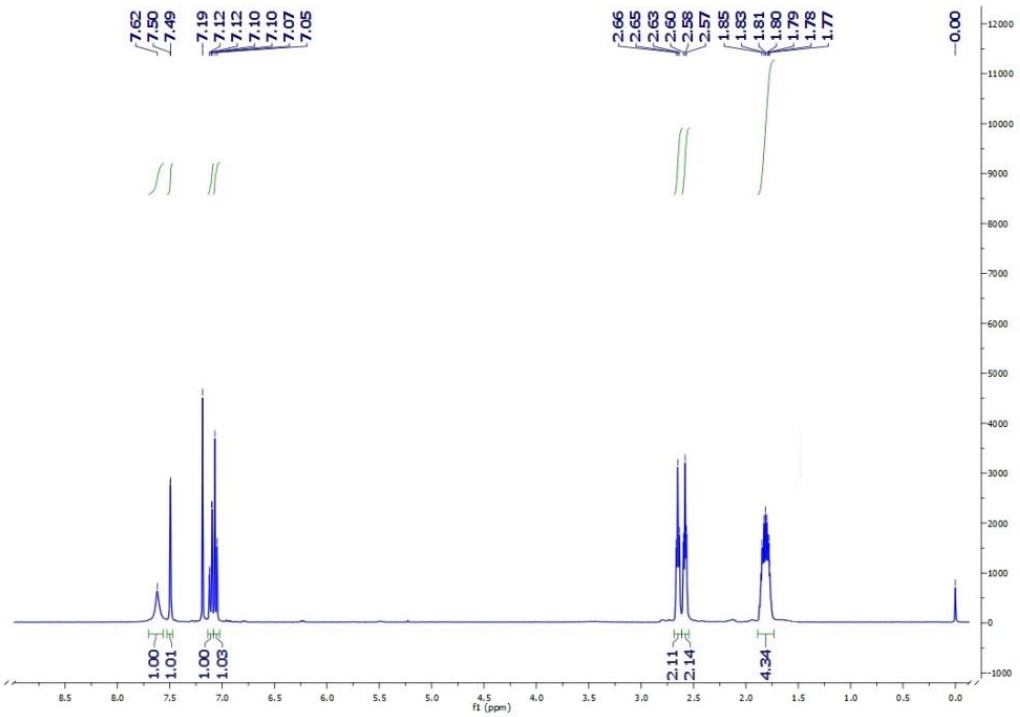

Figure S1j: ^{1}HNMR spectra of HxBr4 in $CDCl_3$

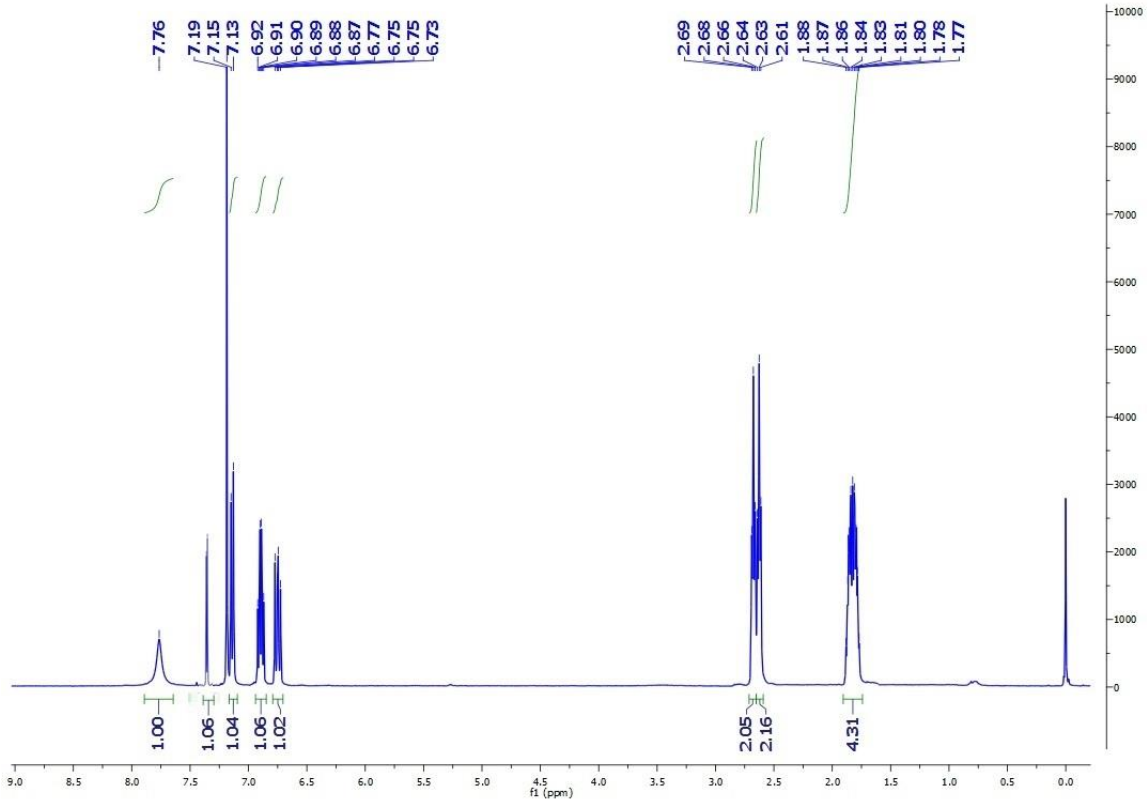

Figure S1k: ^{1}HNMR spectra of HpP in $CDCl_3$

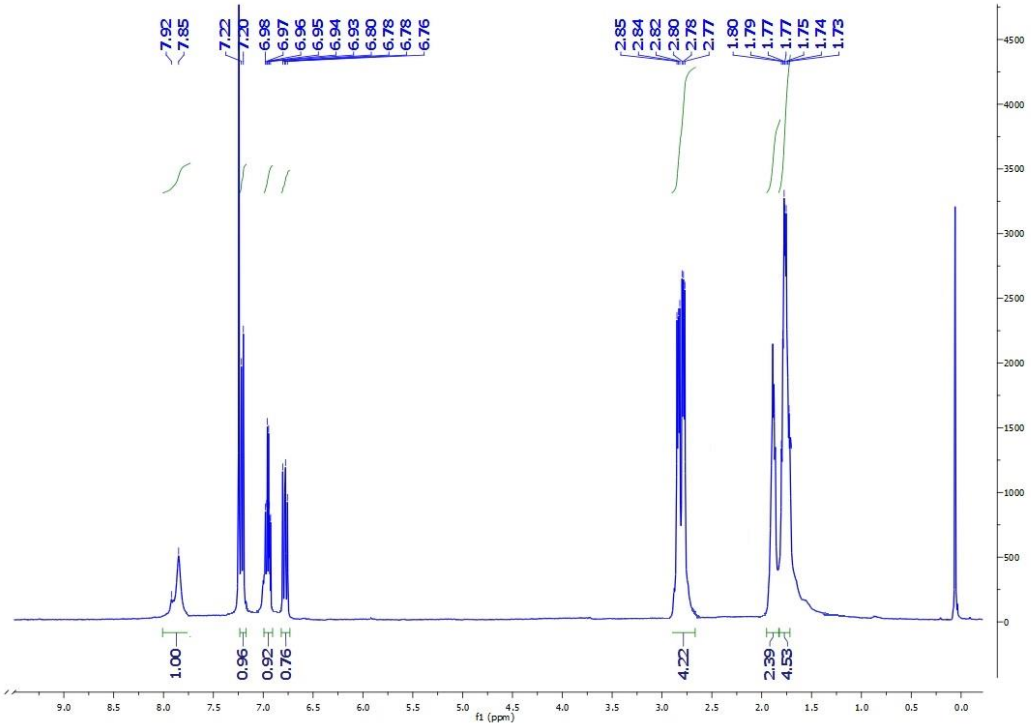

Figure S1l: ^{1}HNMR spectra of HpF2 in $CDCl_3$

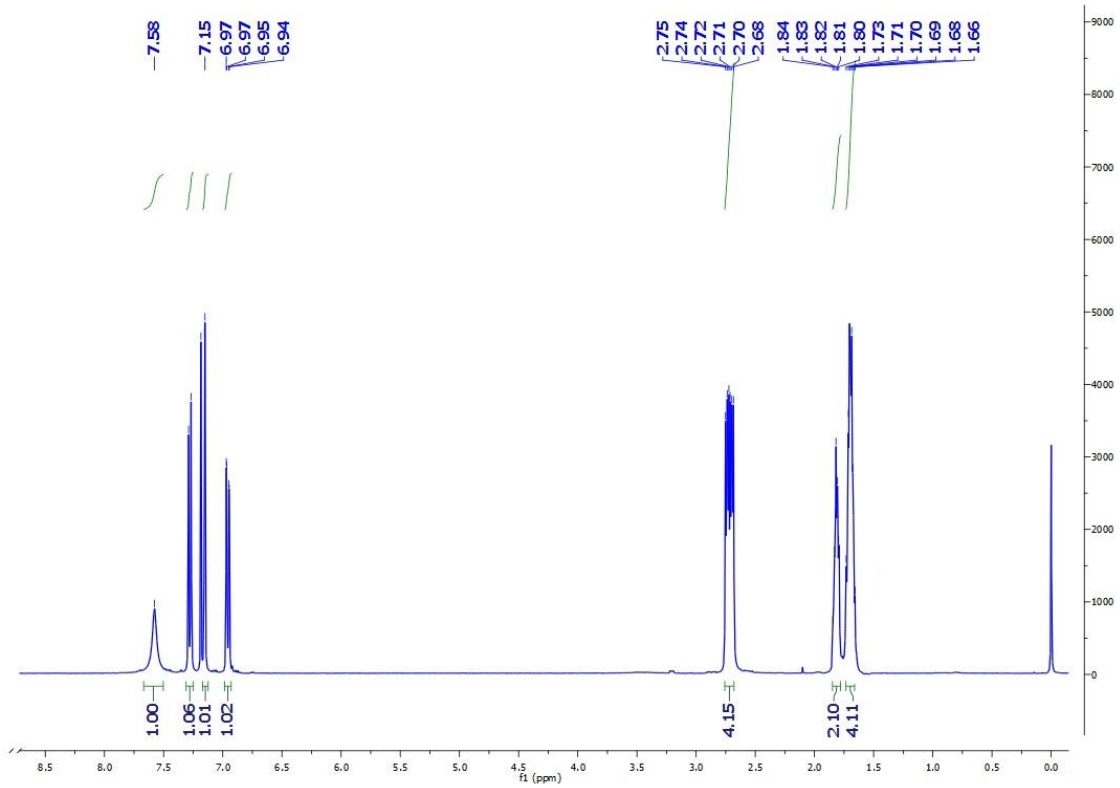

Figure S1m: ^{1}HNMR spectra of HpF3 in $CDCl_3$

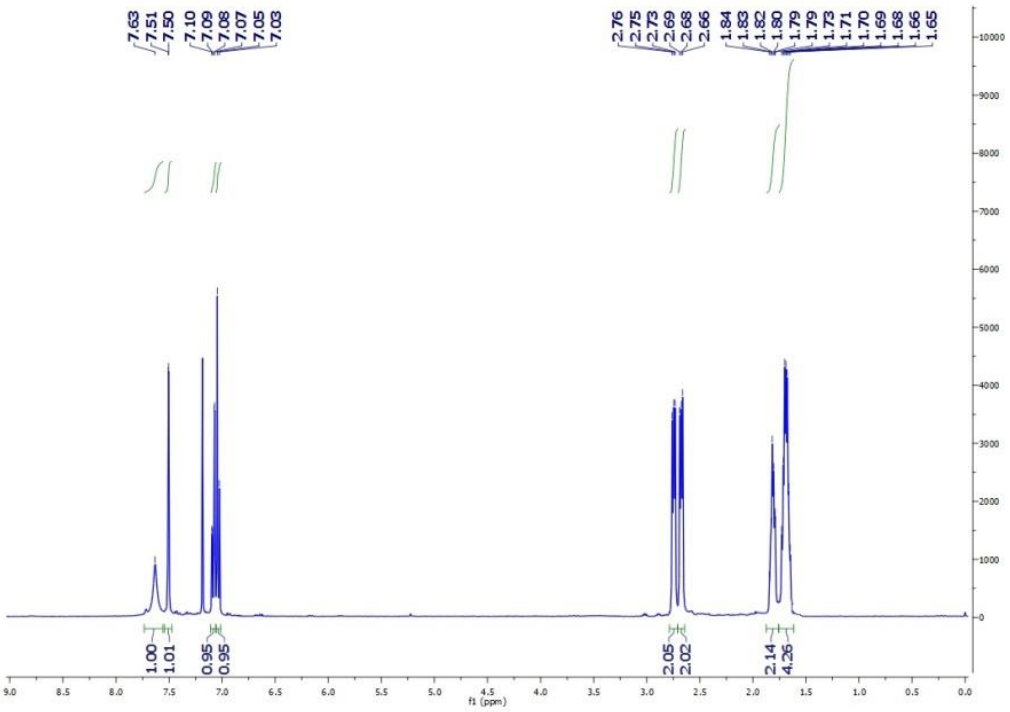

Figure S1n: ^{1}HNMR spectra of HpF4 in $CDCl_3$

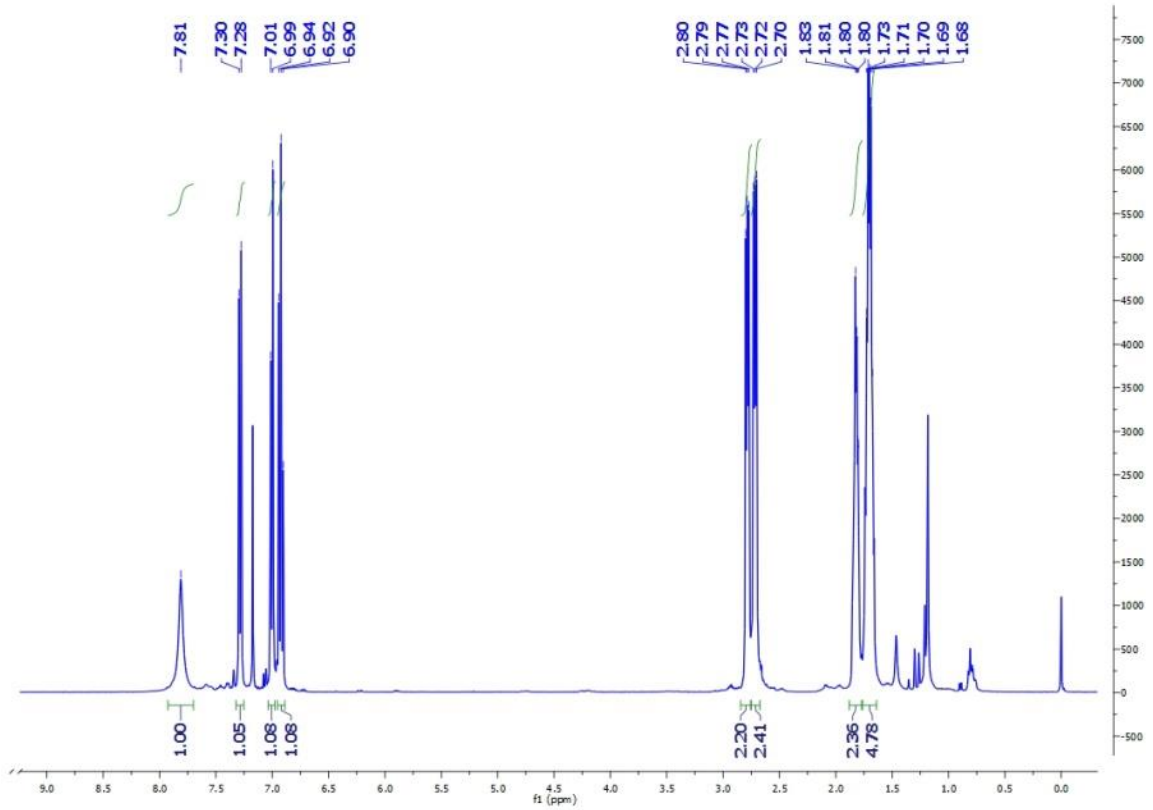

Figure S1o: ^{1}HNMR spectra of HpCl2 in $CDCl_3$

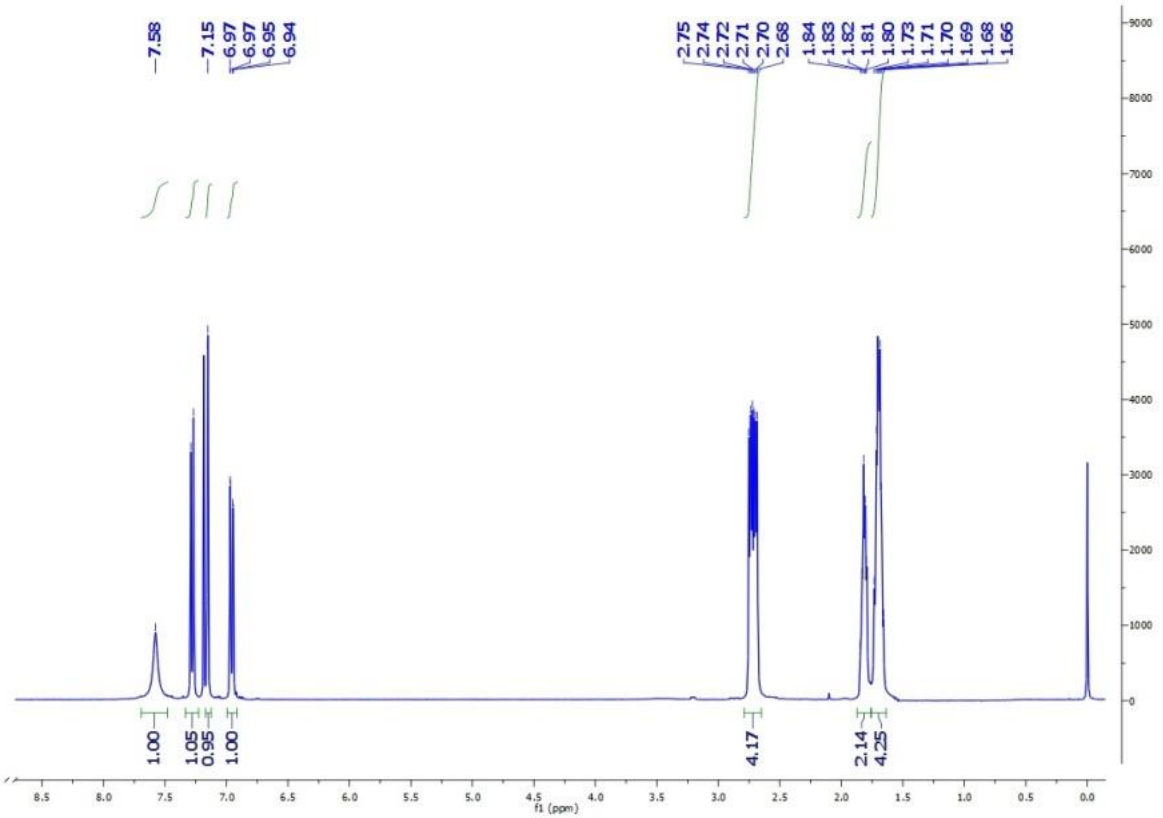

Figure S1p: ^{1}HNMR spectra of HpCl3 in $CDCl_3$

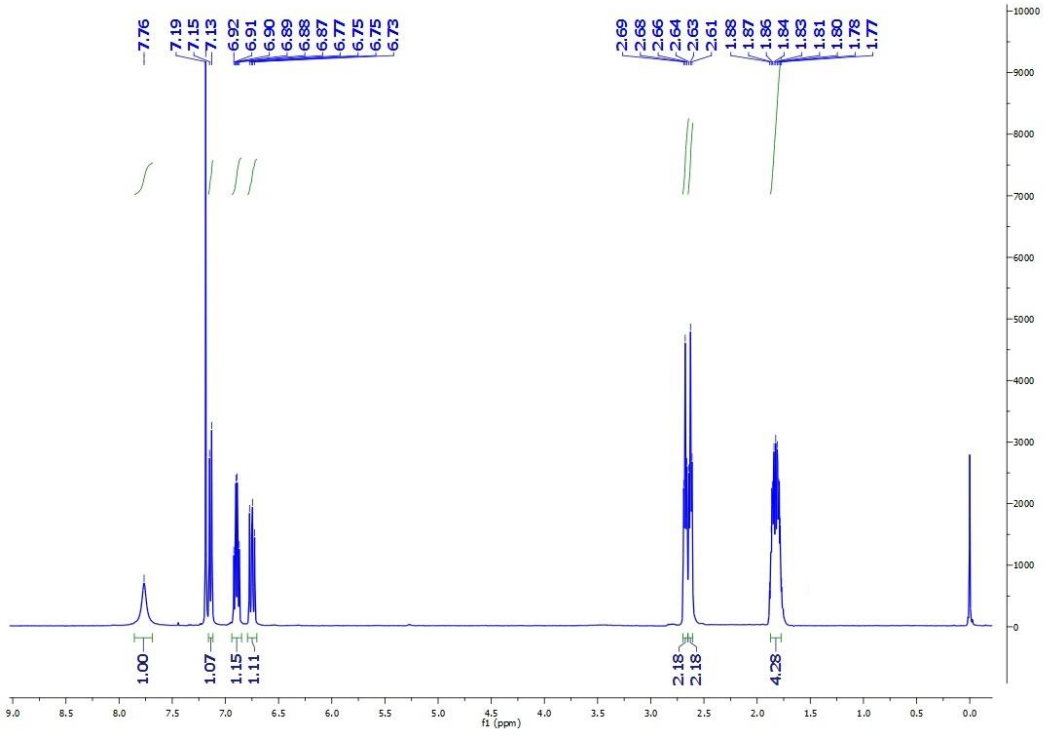

Figure S1q: ^{1}HNMR spectra of HpCl4 in $CDCl_3$

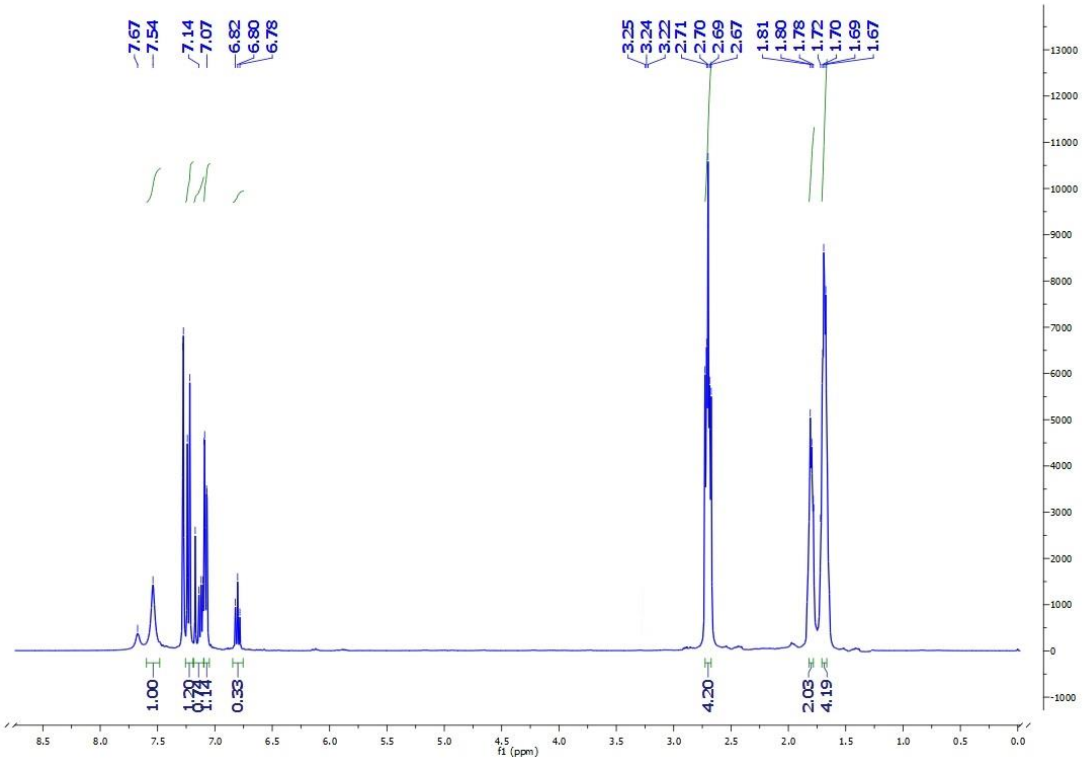

Figure S1r: ^{1}HNMR spectra of HpBr2 in $CDCl_3$

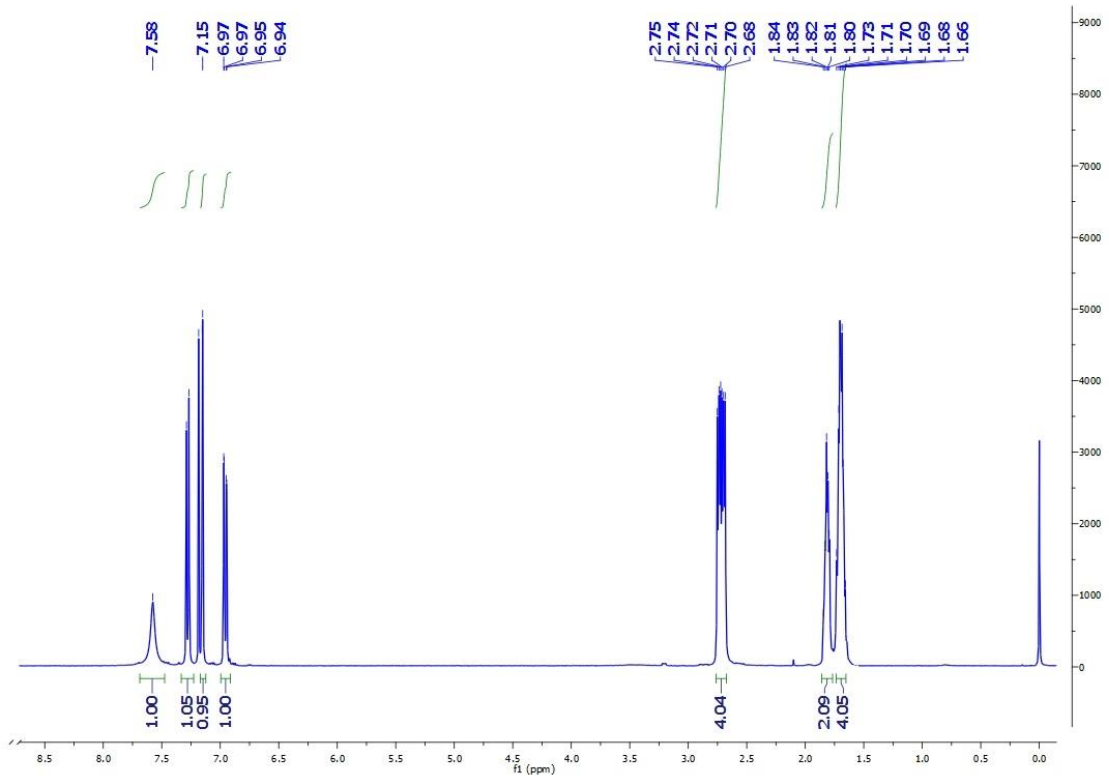

Figure S1s: ^{1}HNMR spectra of HpBr3 in $CDCl_3$

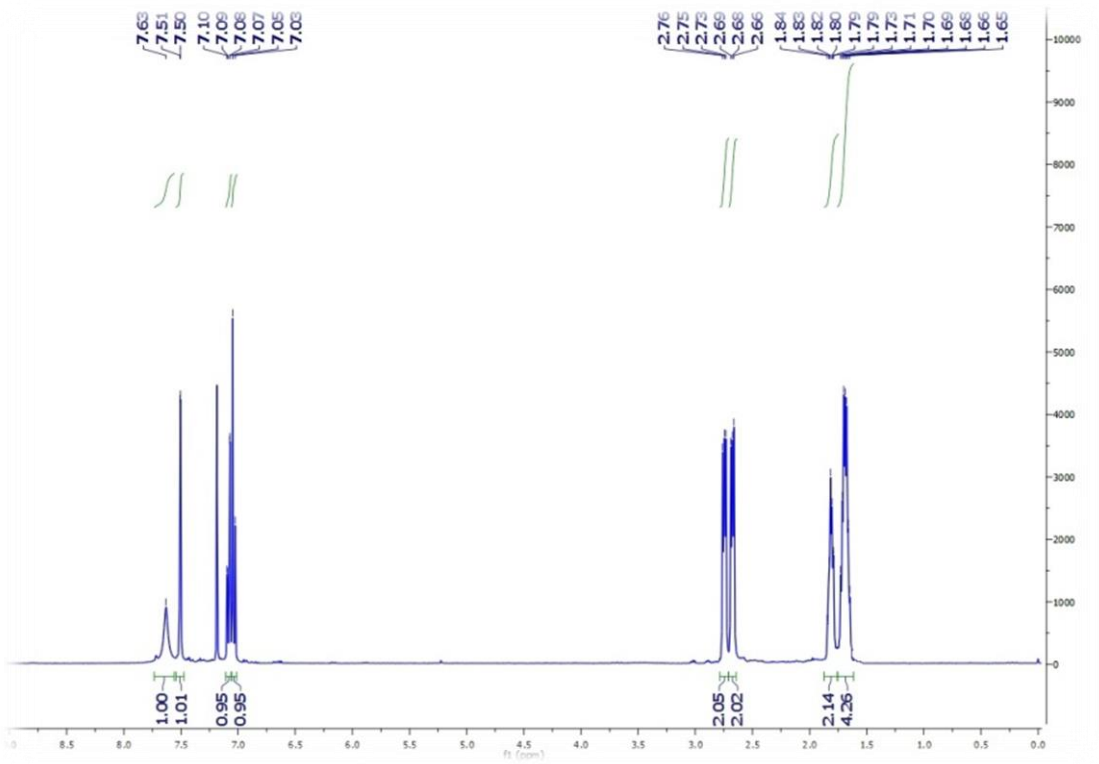

Figure S1t: ^{1}HNMR spectra of HpBr4 in $CDCl_3$

Table S4: Crystallization conditions of all the solid compounds.

	Sample Code	**Solvent/Condition**	**Temperature**	**Results**
1	HxP	Ethanol, Hexane	RT	Crystal was obtained
		Ether, DCM, Ethyl acetate, $CHCl_3$,	5˚C	No crystal was obtained
2	HxF2	Ethanol, Hexane	RT, 5˚C	Crystal was obtained
		Ether, DCM, Ethyl acetate, $CHCl_3$, CH_3CN,Benzene	5˚C	No crystal was obtained
3	HxF3	Ethanol, Hexane	RT, 5˚C	Crystal was obtained
		Ether, DCM, Ethyl acetate, $CHCl_3$, CH_3CN,Benzene	5˚C	No crystal was obtained
4	HxF4*	Methanol, Hexane	RT, 5˚C	Crystal was obtained

		Ether, DCM, Ethyl acetate, $CHCl_3$, CH_3CN,Benzene	5˚C	No crystal was obtained
5	HxCl2	Ethanol, Hexane, DCM	RT , 5˚C	Crystal was obtained
		Ether, Ethyl acetate, $CHCl_3$, CH_3CN,Benzene	5˚C	No crystal was obtained
6	HxCl3	Ethanol, Hexane, DCM,	RT, 5˚C	Crystal was obtained
		Ether, Ethyl acetate, $CHCl_3$,CH_3CN,Benzene	5˚C	No crystal was obtained
7	HxCl4	Ethanol, Hexane, DCM,	RT , 5˚C	Crystal was obtained
		Ether, Ethyl acetate, $CHCl_3$,CH_3CN,Benzene,	5˚C	No crystal was obtained
8	HxBr2	Ethanol, Hexane, DCM	RT, 5˚C	Crystal was obtained
		Ether, Ethyl acetate, $CHCl_3$, CH_3CN,Benzene	5˚C	No crystal was obtained
9	HxBr3	Ethanol, Hexane, DCM	RT, 5˚C	No crystal was obtained
		Ether, Ethyl acetate, $CHCl_3$,CH_3CN,Benzene	5˚C	
10	HxBr4	Ethanol, Hexane, DCM	RT, 5˚C	Crystal was obtained
		Ether, Ethyl acetate, $CHCl_3$, CH_3CN,Benzene	5˚C	No crystal was obtained
11	HpP	liquid		---
12	HpF2	Ethanol, Hexane	RT, 5˚C	Crystal was obtained
		Ether, DCM, Ethyl acetate, $CHCl_3$,CH_3CN,Benzene	5˚C	No crystal was obtained
13	HpF3	Ethanol, Hexane, DCM,	RT, 5˚C	Crystal was obtained
		Ether, Ethyl acetate, $CHCl_3$, CH_3CN,Benzene	5˚C	No crystal was obtained

14	HpF4	Ethanol, Hexane, DCM,	RT, 5˚C	Crystal was obtained
		Ether, Ethyl acetate, $CHCl_3$, CH_3CN,Benzene	5˚C	No crystal was obtained
15	HpCl2	Ethanol, Hexane, DCM,	RT, 5˚C	Crystal was obtained
		Ether, Ethyl acetate, $CHCl_3$, CH_3CN,Benzene	5˚C	No crystal was obtained
16	HpCl3	Methanol	RT, 5˚C	Crystal was obtained
		Ether, Ethyl acetate, $CHCl_3$, ,CH_3CN,Benzene	5˚C	No crystal was obtained
17	HpCl4	Ethanol, Hexane, DCM	RT , 5˚C	Crystal was obtained
		Ether, Ethyl acetate, $CHCl_3$, CH_3CN,Benzene	5˚C	No crystal was obtained
18	HpBr2	Ethanol, Hexane	RT, 5˚C	Crystal was obtained
		Ether, DCM, Ethyl acetate, $CHCl_3$, CH_3CN,Benzene,	5˚C	No crystal was obtained
19	HpBr3	Ethanol, Hexane	RT, 5˚C	Crystal was obtained
		Ether, DCM, Ethyl acetate, $CHCl_3$, CH_3CN,Benzene,	5˚C	No crystal was obtained
20	HpBr4	Ethanol, Hexane	RT, 5˚C	Crystal was obtained
		Ether, DCM, Ethyl acetate, $CHCl_3$, ,CH_3CN,Benzene	5˚C	No crystal was obtained

* Polymorphs were obtained in this case

Table S5: Crystallographic and Refinement data

DATA	HxP	HxF2	HxF3	HxCl2	HxCl3	HxCl4	HxBr3	HxBr4

Formula	$C_{12}H_{13}N$	$C_{12}H_{12}FN$	$C_{12}H_{12}FN$	$C_{12}H_{12}ClN$	$C_{12}H_{12}ClN$	$C_{12}H_{12}ClN$	$C_{12}H_{12}BrN$	$C_{12}H_{12}BrN$
Formula Weight	171.23	189.23	189.23	205.68	205.68	205.68	250.14	250.14
CCDC No.	1827363	1827364	1827365	1827368	1827369	1827370	1827371	1827372
Crystal System;	Orthorhombic	Monoclinic;	Orthorhombic;	Orthorhombic;	Monoclinic;	Monoclinic;	Orthorhombic	Monoclinic;
Space group	$P2_12_12_1$	$C2/c$	$P2_12_12_1$	$Pbca$	$P2_1$	$C2/c$	$Pbca$	$C2/c$
***a* (Å)**	6.1147(4)	17.4633(7)	6.1937(6)	10.8001(9)	5.713(1)	24.458(1)	10.179(2)	24.4539(18)
***b* (Å)**	7.9668(5)	11.1118(7)	7.4492(8)	8.8083(7)	8.112(2)	6.0867(3)	8.763(2)	6.1680(4)
***c* (Å)**	19.4856(13)	9.6718(4)	19.920(2)	21.041(2)	10.878(2)	16.309 (1)	22.946(4)	16.235 (1)
α (⁰)/ β (⁰)/ γ (⁰)	90, 90, 90	90, 91.282(3), 90	90, 90, 90	90, 90, 90	90, 96.698(8), 90	90, 125.800(3), 90	90, 90, 90	90, 124.277(2), 90
Volume (Å^3)/	949.23(11)/	1876.33(16)/	919.1(2)/	2001.6(3)/	500.7(2)/	1969.2(2)/	2046.7(6)/	2023.5(2)/
Density (g/cm^3)	1.198	1.340	1.368	1.365	1.364	1.388	1.624	1.642
Z/ Z'	4/1	8/ 1	4/ 1	8/ 1	2/ 1	8/ 1	8/ 1	8/ 1
F (000)/ μ (mm^{-1})	368/0.070	800/ 0.092	400/0.094	864/ 0.337	216/ 0.337	864/ 0.343	1008/ 3.973	1008/ 4.019
θ (min, max)	2.76, 27.54	2.33, 30.60	2.92/30.55	2.70, 30.55	3.14, 24.96	2.51, 30.55	2.68, 30.77	3.04, 30.53
$h_{min,max}$, $k_{min,max}$, $l_{min,max}$	-7, 7; -10, 10; -25, 25	-24, 20; -15, 15; -13, 12	-8, 8; -8, 10; -28, 28	-15, 15; -12, 12; -30, 25	-6, 6; -9, 9; -12, 12	-34, 34; -6, 8; -23, 22	-14, 12; -12, 12; -32, 32	-34, 34; -8, 6; -23, 23
No. of ref.	23905	13542	13579	17748	4608	16814	22551	16811
No. unique ref./ obs. ref.	2179/1530	2870/ 2491	2806/ 2449	3058/2457	1681/ 1561	3002/ 2601	3171/ 1976	3082/ 2685
No. of parameters	119	127	127	128	146	146	127	146
R_all, R_obs	0.0926, 0.0557	0.0522, 0.0443	0.0548, 0.0437	0.0548, 0.0399	0.0378, 0.0327	0.0442, 0.0365	0.1031, 0.0490	0.0332, 0.0266
wR_2_all, wR_2_obs	0.1423, 0.1253	0.1218, 0.1164	0.1087, 0.1035	0.1089, 0.1013	0.0779, 0.0762	0.1011, 0.0968	0.1335, 0.1120	0.0712, 0.0680
$\Delta\rho_{min,max}$(eÅ^{-3})	-0.179, 0.173	-0.316, 0.365	-0.263, 0.381	-0.351, 0.481	-0.174, 0.197	-0.325, 0.431	-0.796, 0.757	-0.522, 0.403
G. o. F	1.073	1.034	1.070	1.040	1.086	1.066	1.018	1.059

Table S5: continued….

DATA	**HPF2**	**HPF4**	**HPCl2**	**HpCl3**	**HPCl4**	**HPBr2**	**HPBr3**	**HPBr4**
Formula	$C_{13}H_{14}FN$	$C_{13}H_{14}FN$	$C_{13}H_{14}ClN$	$C_{13}H_{14}ClN$	$C_{13}H_{14}ClN$	$C_{13}H_{14}BrN$	$C_{13}H_{14}BrN$	$C_{13}H_{14}BrN$
Formula Weight	203.25	203.25	219.70	219.70	219.70	264.16	264.16	264.16
CCDC No.	1827374	1827375	1827376	1827377	1827378	1827379	1827380	1827381
Crystal System;	Orthorhombic;	Monoclinic;	Monoclinic;	Monoclinic;	Monoclinic;	Monoclinic;	Orthorhombic;	Monoclinic;
Space group	$Pbcn$	$P2_1/n$	$P2_1/c$	$P2_1$/c	$P2_1/n$	$P2_1/c$	$Pbcn$	$P2_1/c$
***a* (Å)**	11.958(1)	9.8202(6)	8.688 (2)	12.1278(11)	9.8035(5)	8.7856(8)	23.769(4)	9.5400(4)
***b* (Å)**	9.1060(9)	22.010(2)	11.791(2)	8.1084(7)	22.709(1)	11.645(1)	11.2921(19)	6.2063(2)
***c* (Å)**	18.708(2)	9.8725(7)	10.313(2)	11.2668(10)	9.9786(6)	10.640(1)	8.2022(11)	18.8852(8)
α (⁰)/ β (⁰)/ γ (⁰)	90, 90, 90	90, 101.926(3), 90	90, 90.892(5), 90	90,108.995(2), 90	90, 101.405(2), 90	90, 90.470(4), 90	90, 90, 90	90, 98.474(1), 90
Volume (Å^3)	2037.1(3)	2087.8(2)	1056.3(3)	1047.61(16)	2177.7(2)	1088.6(2)	2201.5(6)	1105.95(7)
Density (g/cm^3)	1.325	1.293	1.382	1.393	1.340	1.612	1.594	1.587
Z/ Z'	8/1	8/2	4/1	4/1	8/2	4/1	8/1	4/1
F (000)/ μ (mm^{-1})	864/ 0.090	864/ 0.088	464/ 0.324	464/ 0.327	928/ 0.314	536/ 3.740	1072/ 3.699	536/ 3.681
θ (min, max)	2.76, 30.56	2.30, 30.58	2.62, 26.37	3.08, 30.50	2.30, 30.59	2.59, 24.99	3.14, 24.99	2.83, 30.51

$h_{min,max}$, $k_{min,max}$, $l_{min,max}$	-16, 17; -12, 13; -26, 26	-14, 14; -31, 31; -14, 14	-10, 10; -14, 13, -12, 12	-17, 16; -9, 11; -16, 15	-13, 14; -32, 32, -14, 14	-10, 10; -12, 13; -12, 11	-25, 28; -10, 13; -9, 8	-13, 13; -8, 6; -26, 26
No. of ref.	40673	37051	9349	9700	30504	8642	8659	15446
No. unique ref./ obs. Ref.	3125/ 2724	6387/ 5327	2155/ 1427	3176/ 2619	6657/ 5351	1924/ 1719	1938/ 1763	3369/ 2972
No. of parameters	136	271	136	136	271	136	136	136
R_all, R_obs	0.0493, 0.0419	0.0571, 0.0463	0.1067, 0.0586	0.0484, 0.0374	0.0574, 0.0403	0.0450, 0.0403	0.0434, 0.0386	0.0306, 0.0244
wR_2_all, wR_2_obs	0.1124, 0.1074	0.1265, 0.1190	0.1447, 0.1263	0.0977, 0.0925	0.0965, 0.0898	0.1002, 0.0975	0.0968, 0.0953	0.0602, 0.0577
$\Delta\rho_{min,max}$(E$Å^{-3}$)	-0.225, 0.398	-0.285, 0.456	-0.420, 0.772	-0.253, 0.453	-0.287, 0.420	-0.952, 1.059	-0.323, 0.532	-0.550, 0.358
G. o. F	1.033	1.042	1.055	1.041	1.031	1.080	1.368	1.110

Section 4: Structural details

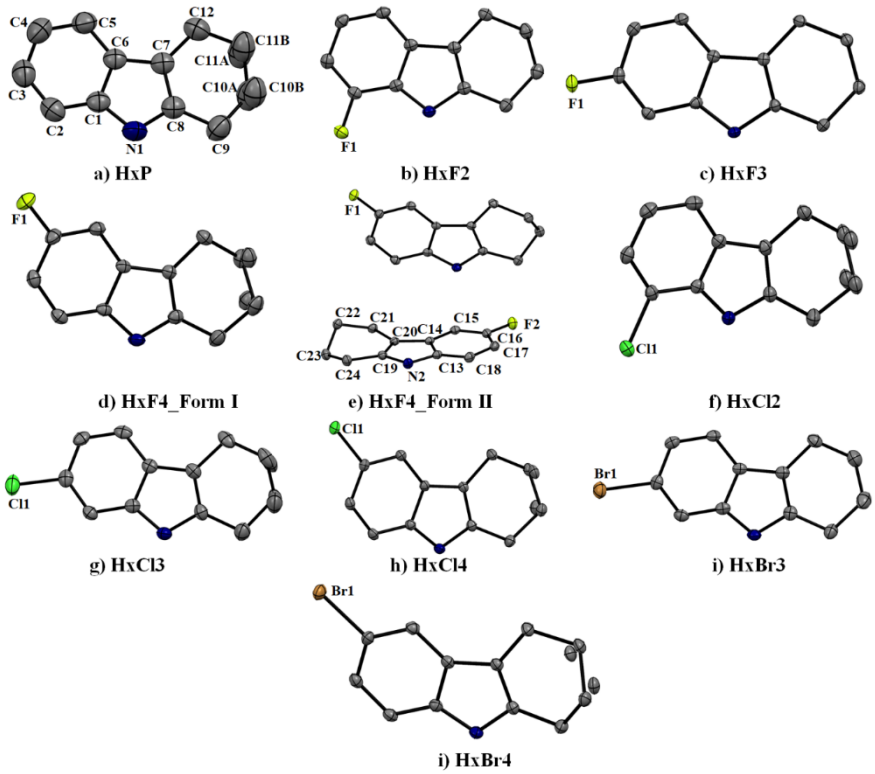

Figure S2a: *ORTEP*s of **series Hx** drawn at 50% ellipsoidal probability with their sample code and numbering scheme.

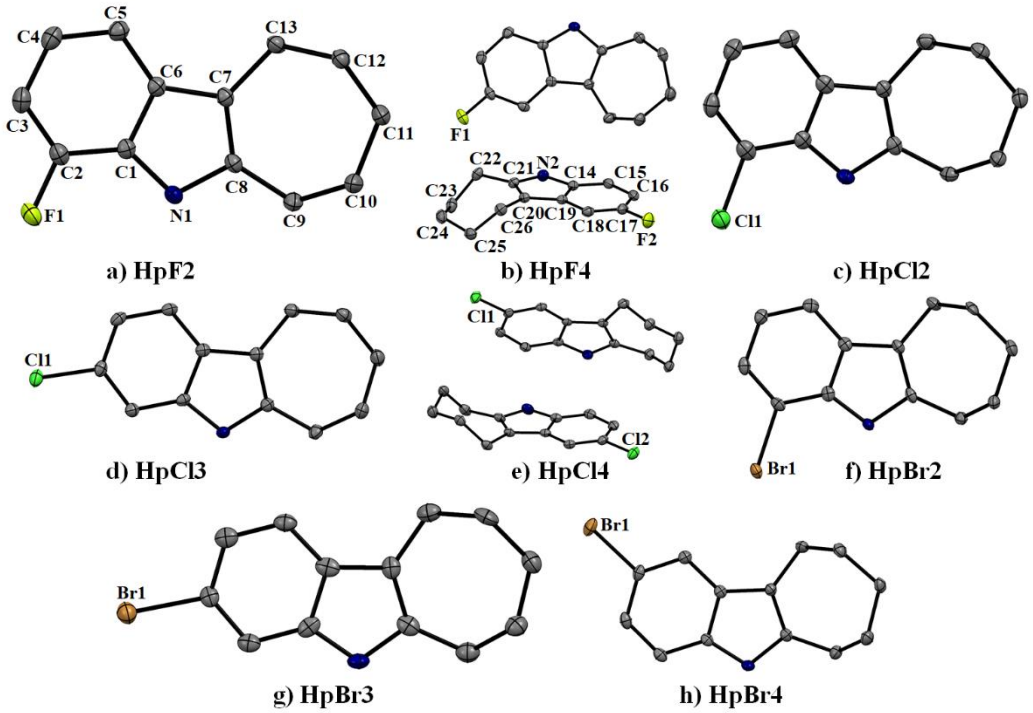

Figure S2b: *ORTEP*s of **series Hp** drawn at 50% ellipsoidal probability with their sample code and numbering scheme.

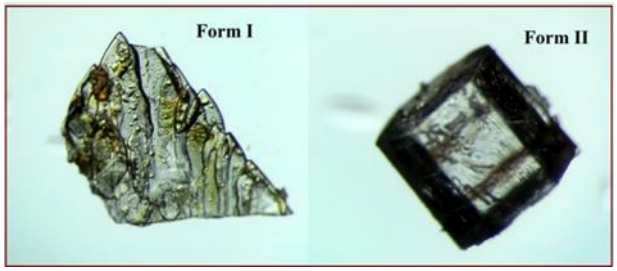

Figure S3: Morphology of the crystals of two polymorphic forms of HxF4

Table S6: Crystallographic and Refinement data of the two polymorphs

DATA	**HxF4_Form I**	**HxF4_Form II**
Formula	$C_{12}H_{12}NF$	$C_{12}H_{12}NF$
Formula Weight	189.23	189.23
Solvent	Methanol, RT	Hexane, LT (5ºC)
Morphology	Plate	Block
CCDC No.	1827366	1827367
Crystal System, Space group	Orthorhombic, $P2_12_12_1$	Monoclinic, $P2_1/n$
***a* (Å)**	6.0226(4)	10.5411(11)

***b* (Å)**	7.8459(6)	8.1081(8)
***c* (Å)**	20.1968(14)	21.980(2)
α (⁰)/ β (⁰)/ γ (⁰)	90, 90, 90	90, 98.610(2), 90
Volume (Å^3) /Density (g/cm^3)	954.35(12), 1.317	1857.4(3), 1.353
Z/ Z'	4/1	8/2
F (000)/ μ (mm^{-1})	400/ 0.091	800/ 0.093
θ (min, max)	2.79, 30.57	2.29, 30.62
$h_{min,max}$, $k_{min,max}$, $l_{min,max}$	-8, 8; -11, 10; -28, 28	-13,15; -11, 11; -29, 31
No. of ref.	25718	24992
No. unique ref./ obs. ref.	2928/ 2429	5693/ 4862
No. of parameters	146	253
R_all, R_obs	0.0638, 0.0473	0.0545, 0.0457
wR_2_all, wR_2_obs	0.1156, 0.1088	0.1215, 0.1165
$\Delta\rho_{min,max}$(eÅ^{-3})	-0.286, 0.282	-0.261, 0.448
G. o. F	1.029	1.045

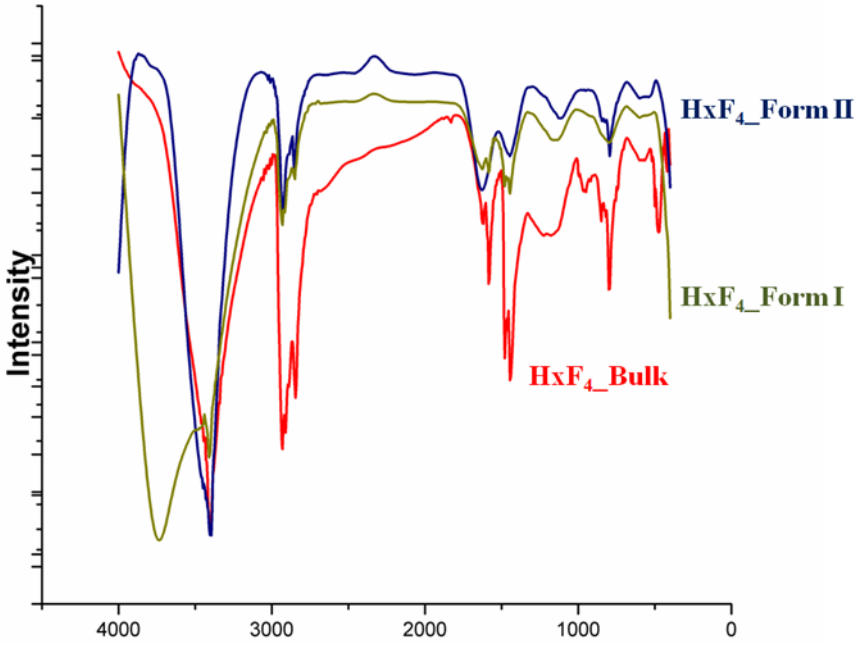

Figure S4: Overlay of IR spectra of two forms of **HxF_4** with that of a bulk powder.

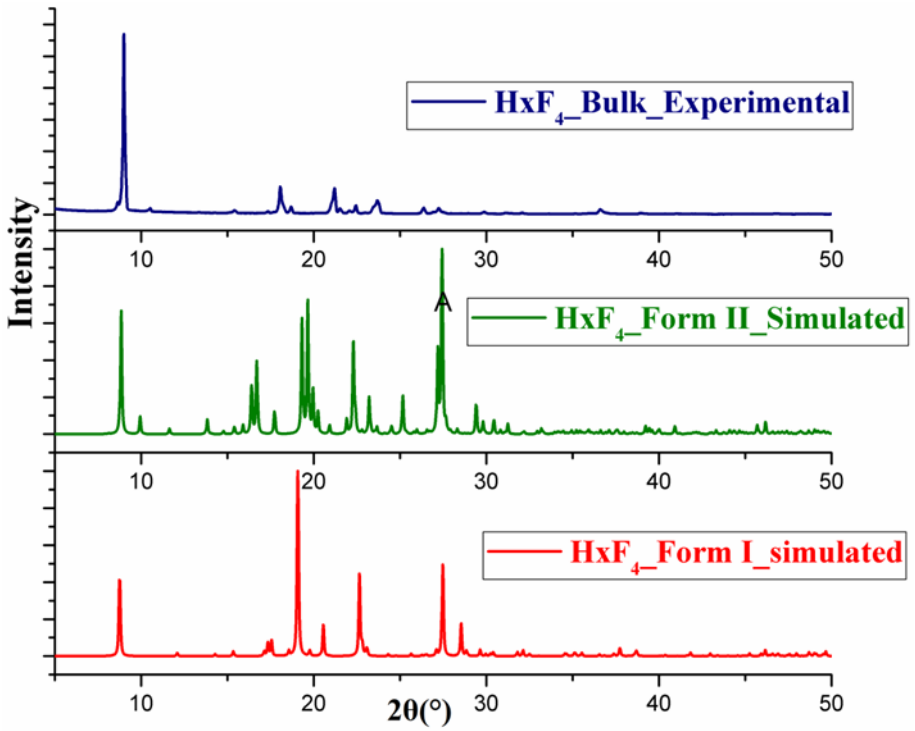

Figure S5: Overlay of simulated powder XRD spectra of two forms of **HxF₄** with the experimental powder pattern of bulk powder.

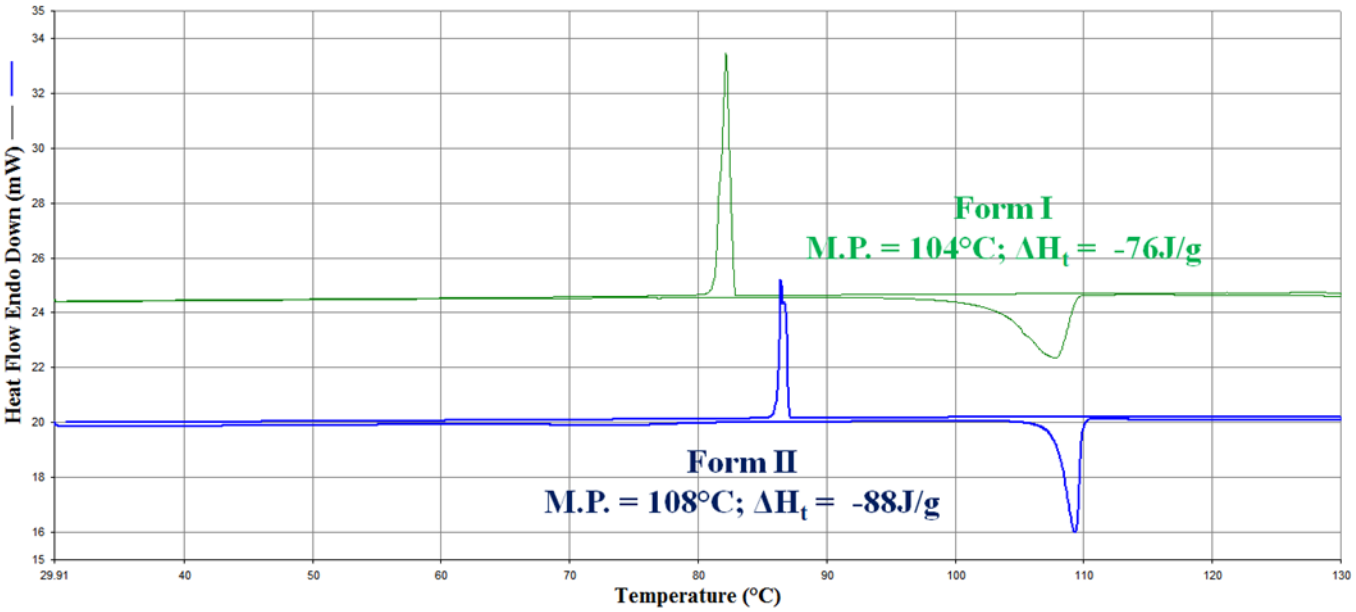

Figure S6: Overlay of the DSC traces of two forms of **HxF₄**. Colour code: Green represents **form I** while blue is for **form II** (one heating and one cooling cycle are shown for each of the two forms).

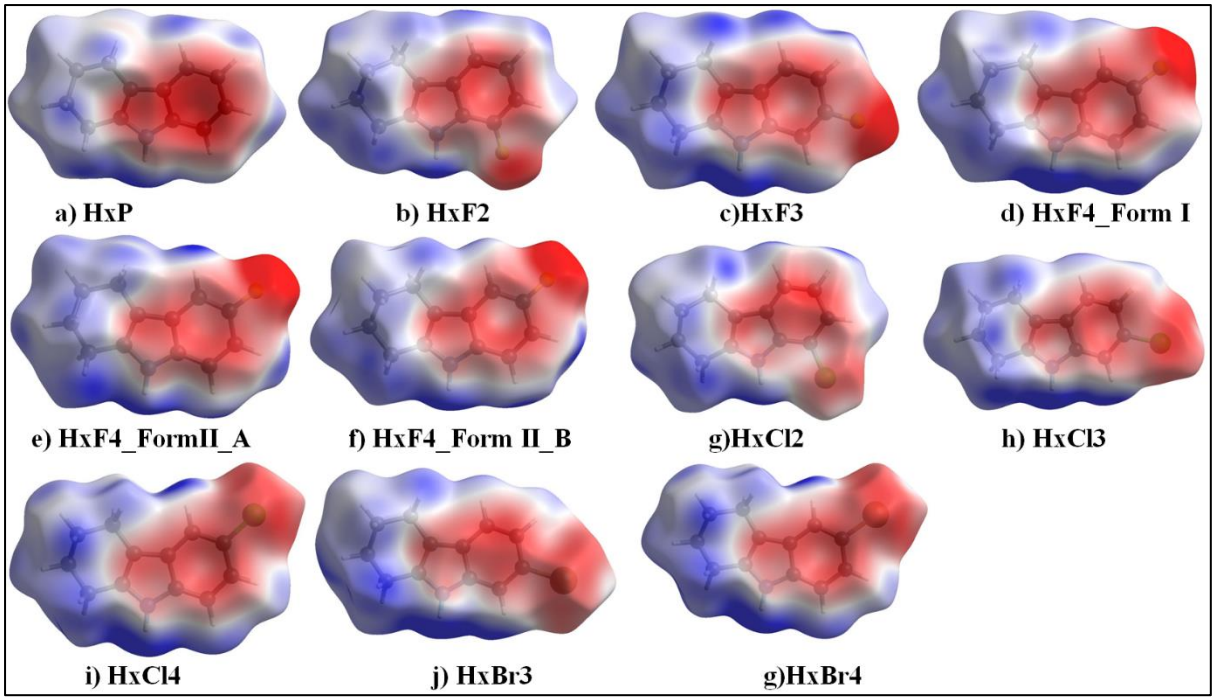

Figure S7a: Molecular electrostatic potential maps of the crystal structures of the Hx series plotted on the Hirshfeld surface at ±0.04 au contour level.

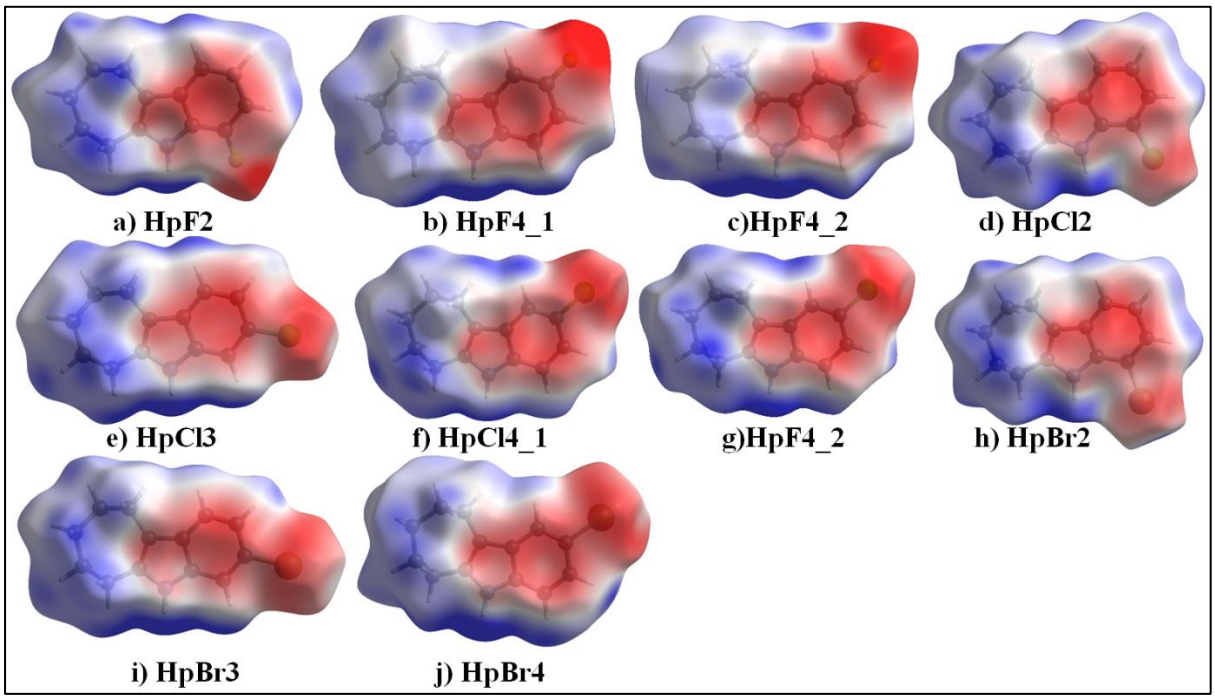

Figure S7b: Molecular electrostatic potential maps of the crystal structures of the Hp series plotted on the Hirshfeld surface at ±0.04 au contour level.

Table S7: Lattice energies of all the crystal structures partitioned into different energy components

Molecule	E_{coul} kJ/mol	E_{pol} kJ/mol	E_{disp} kJ/mol	E_{rep} kJ/mol	E_{tot} kJ/mol
HxP	-32.4	-17.8	-116.4	70.4	-96.2
HxF2	-35.3	-23.0	-123.8	85.7	-96.4
HxF3	-38.5	-20.2	-133.0	91.9	-99.8
HxF4_Form I	-42.2	-21.9	-121.5	88.8	-97.2
HxF4_Form II	-39.6	-25.9	-130.2	93.0	-102.6
HxCl2	-32.3	-22.4	-145.4	97.1	-103.0
HxCl3	-47.0	-26.3	-145.3	103.7	-115.2
HxCl4	-41.2	-23.5	-151.8	100.9	-115.6
HxBr3	-46.8	-24.4	-145.1	102.9	-113.4
HxBr4	-39.9	-22.0	-149.0	98.8	-112.0
HpF2	-37.8	-22.2	-136.8	94.3	-102.4
HpF4	-40.0	-22.2	-131.3	91.6	-101.9
HpCl2	-38.6	-22.8	-162.3	108.4	-115.4
HpCl3	-41.5	-28.5	-167.5	109.9	-127.7
HpCl4	-45.9	-25.1	-154.7	106.8	-118.9
HpBr2	-39.1	-20.9	-157.3	108.2	-109.1
HpBr3	-48.7	-24.3	-156.6	106.3	-123.3
HpBr4	-44.2	-23.3	-154.4	102.8	-119.2

Table S8: List of intermolecular interactions present in reported structures along with geometrical parameters and interaction energies.

Motif	Symmetry	Centroid distance	E_{coul} kJ/mol	E_{pol} kJ/mol	E_{disp} kJ/mol	E_{rep} kJ/mol	E_{tot} kJ/mol	Intermolecular Interactions	Geometry Å/°/°
	HxP								
I	0.5+x,-0.5-y,1-z	5.215	-16.4	-10.3	-37.0	28.2	-35.4	N1-H1⋯C2(π) C2(sp^2)-H2⋯C8(π)	2.73/171 2.84/161
II	0.5+x,0.5-y,1-z	5.161	-6.1	-3.6	-30.5	19.3	-20.9	C12(sp^3)-H12B⋯C6(π) C5(sp^2)-H5⋯C7(π)	2.89/154 3.05/153
III	1+x,y,z	6.107	-5.5	-2.2	-18.2	10.2	-15.7	Molecular stacking	
IV	2-x,-0.5+y,0.5-z	9.280	-0.9	-0.4	-8.6	3.7	-6.3	C9-H9A⋯H11B-C11A	2.62/136/122
V	2.5-x,-y,-0.5+z	10.151	-1.6	-0.6	-7.7	4.1	-5.8	C3-H3⋯H10B-C10A	2.76/124/135
VI	1.5-x,-y,-0.5+z	10.238	-1.4	-0.6	-8.6	4.9	-5.7	C4-H4⋯H10B-C10A	2.53/150/110
	HxF2								
I	x,-y,0.5+z	5.454	-18.4	-12.5	-31.4	27.4	-34.9	N1-H1⋯C4(π) C9(sp^3)-H9B⋯C7(π)	2.50/164 3.07/134

II	1.5-x,0.5-y,1-z	4.039	-14.5	-8.9	-56.2	47.9	-31.8	C10(sp^3)-H10A···C3(π)	2.75/166
III	1.5-x,-0.5+y,1.5-z	5.969	-2.3	-2.2	-19.7	11.2	-13.0	C5-H5···N1 C12-H12B···F1	2.82/151 2.71/120
IV	1.5-x,0.5-y,2-z	7.642	-2.6	-1.0	-13.5	6.6	-10.6	Molecular stacking	
V	1-x,-y,1-z	9.258	-2.9	-1.8	-17.4	12.6	-9.4	H10B···H11B	2.46/147/132
VI	2-x,y,1.5-z	9.116	-3.3	-1.5	-11.4	8.8	-7.3	C3-H3···F1	2.66/149
VII	1-x,y,1.5-z	8.883	-1.7	-0.8	-10.7	6.4	-6.8	C12-H12B···H11A-C11	2.63/143/127
VIII	-0.5+x,0.5-y,-0.5+z	10.342	-1.2	-0.7	-8.3	4.4	-5.8	C11-H11A···H4-C4	2.504/142/134
	HxF3								
I	-0.5+x,-0.5-y,1-z	4.816	-17.6	-10.2	-40.9	32.4	-36.2	N1-H1···C2(π) C2(sp^2)-H2···C8(π) C10-H10A···F1 C9-H9B···F1	2.79/159 2.88/154 2.84/164 2.88/153
II	0.5+x,0.5-y,1-z	4.948	-11.0	-5.3	-38.8	30.9	-24.3	C5-H5···C7(π) C12(sp^3)-H12B···C5(π)	2.98/143 2.97/146
III	1+x,y,z	6.194	-5.1	-3.2	-20.6	12.3	-16.6	C12-H12A···N1 Molecular stacking	2.94/137
IV	1.5-x,-y,0.5+z	10.421	-3.0	-1.3	-9.1	6.8	-6.6	C11-H11B···F1	2.76/154
V	2-x,0.5+y,1.5-z	10.070	-1.2	-0.8	-11.1	6.6	-6.5	C9-H9B···H11B-C11	2.63/138/122
VI	2.5-x,-y,0.5+z	10.440	-2.6	-0.8	-5.8	3.0	-6.3	C10-H10B…F1 C9-H9A···F1	2.71/131 2.83/112
	HxF4_Form I								
I	0.5+x,0.5-y,1-z	5.031	-19.3	-12.9	-41.8	37.9	-36.1	N1-H1···C6(π) C6(sp^2)-H6···C7(π) C6-H6···N1	2.65/173 2.71/159 2.93/160
II	-0.5+x,-0.5-y,1-z	4.984	-10.9	-4.3	-31.1	23.8	-22.5	C11-H11B···F1 C3(sp^2)-H3···C8(π) C9(sp^3)-H9A···C6(π)	2.46/165 2.97/152 2.96/163
III	1+x,y,z	6.023	-5.6	-2.9	-20.9	14.1	-15.2	C9-H9B···N1 Molecular stacking	2.90/156
IV	2-x,-0.5+y,0.5-z	10.111	-0.4	-0.4	-8.2	2.8	-6.1	C10A-H10B···H12A-C12	2.69/132/137
V	1.5-x,-y,0.5+z	10.444	-3.4	-1.2	-7.9	6.3	-6.1	C5-H5···H11A-C11	2.40/132/121
VI	2.5-x,-y,-0.5+z	10.643	-2.3	-0.9	-5.9	3.5	-5.7	C11A-H11A···F1	2.70/128
	HxF4_Form II								
I	x,y,z	5.197 1…2	-21.6	-15.3	-40.4	39.2	-38.0	N1-H1···C15(π) C6(sp^2)-H6···C20(π)	2.52/171 2.77/157
II	x,1+y,z	5.278	-18.3	-12.6	-34.2	29.9	-35.2	N2-H2···C3(π)	2.53/177

		1…2						C18(sp^2)-H18···C8(π)	2.95/147
III	1-x,-y,-z	3.711 2…2	-11.4	-8.8	-59.4	46.8	-32.7	π…π C(sp^3)21-H21A···C18(π) C24-H24B…F2	 2.87/143 2.88/121
IV	1.5-x,-0.5+y,0.5-z	4.929 1…1	-14.7	-6.4	-40.1	34.5	-26.7	C3(sp^2)-H3···C7(π) C10-H10B···F1 C12-H12B···F1	2.75/168 2.61/147 2.67/141
V	1-x,1-y,-z	6.127 2…2	-5.2	-2.0	-16.6	8.1	-15.8	C21-H21B…F2 Molecular stacking	2.64/143
VI	1-x,1-y,-z	5.681 1…2	-2.4	-3.4	-25.6	16.2	-15.2	C15(sp^2)-H15···C1(π)	3.01/159
VII	1.5-x,0.5+y,0.5-z	6.088 1…2	-2.1	-1.4	-15.5	4.7	-14.2	C9-H9A···N2	3.05/141
VIII	0.5-x,0.5+y,0.5-z	9.600 1…2	-3.4	-1.5	-9.9	5.9	-8.9	C24-H24A···F1 C22-H22B…F1	2.64/130 2.87/122
IX	-1+x,-1+y,z	10.137 2…1	-1.1	-0.7	-10.9	6.6	-6.2	C11-H11B···H23B-C23	2.66/137/105
X	-1+x,y,z	10.541 1…1	-1.1	-0.8	-8.2	4.4	-5.7	C5-H5···H11A-C11	2.59/135/127
	HxCL2								
I	1-x,-y,-z	4.106	-7.6	-7.8	-67.6	50.8	-32.2	π···π stacking	
II	-0.5+x,0.5-y,-z	5.893	-12.4	-8.6	-31.6	25.4	-27.1	N1-H1···C5(π) C12-H12B···Cl1	2.66/157 2.79/142
III	0.5-x,-0.5+y,z	5.800	-7.3	-4.7	-33.9	25.9	-20.0	C4(sp^2)-H4···C2(π)	2.73/148
IV	1-x,1-y,-z	6.192	-7.1	-2.1	-17.2	7.8	-18.7	C9-H9A···Cl1 Molecular stacking	3.06/143
V	x,0.5-y,0.5+z	10.591	-3.8	-1.6	-11.1	8.4	-8.1	C10A-H10B···Cl1	2.89/135
VI	1-x,-0.5+y,0.5-z	9.712	-0.9	-0.9	-11.4	6.0	-7.3	C10A-H10B···H12A-C12	2.48/150/155
	HxCL3								
I	-x,-0.5+y,1-z	4.831	-26.2	-16.0	-45.6	41.1	-46.6	N1-H1···C4(π) C2(sp^2)-H2···C7(π) C11A-H11A···Cl1 C9-H9A···Cl1	2.58/160 2.88/151 2.93/175 2.86/169
II	1-x,-0.5+y,1-z	5.117	-12.5	-6.5	-42.1	35.6	-25.6	C(sp^3)12-H12B···C3(π) C5(sp^2)-H5···C1(π) C5-H5···N1	2.70/137 2.97/162 2.86/165
III	1+x,y,z	5.713	-4.1	-2.8	-23.1	11.0	-18.9	C12-H12A···N1 Molecular stacking	2.79/158

IV	x,y,-1+z	10.878	-3.3	-1.1	-10.2	5.7	-8.8	C9-H9B···Cl1	3.04/126
V	1+x,y,1+z	11.682	-2.7	-1.0	-9.2	6.2	-6.7	C11A-H11B···Cl1	3.20/125
VI	1-x,-0.5+y,2-z	11.414	-0.5	-0.4	-7.7	4.0	-4.5	C10A-H10A···H11A-C11A	2.66/120/116
	HxCL4								
I	0.5-x,0.5+y,0.5-z	4.968	-18.3	-12.5	-47.2	38.6	-39.4	N1-H1···C2(π) C2(sp^2)-H2···C8(π) C9(sp^3)-H9B···C3(π)	2.67/163 2.89/157 2.88/144
II	0.5-x,0.5-y,-z	4.650	-12.3	-5.7	-52.3	33.9	-36.5	C11A(sp^3)-H11A···C6(π)	2.99/141
III	0.5-x,-0.5-y,-z	6.384	-10.2	-5.9	-33.3	29.6	-19.8	C11A(sp^3)-H11B···Cl1	3.15/139
IV	x,1+y,z	6.087	-4.1	-3.6	-24.7	13.1	-19.3	C12-H12A···N1 Molecular stacking	2.97/154
V	-0.5+x,0.5-y,-0.5+z	10.077	-6.6	-2.2	-15.9	13.3	-11.3	C9-H9B···Cl1	2.98/113
VI	1-x,-y,1-z	10.381	-1.1	-1.1	-9.0	3.2	-8.0	C3-H3···Cl1	3.27/151
	HxBr3								
I	1-x,0.5+y,0.5-z	5.085	-21.3	-13.6	-38.4	31.6	-41.7	N1-H1···C5(π) C2(sp^2)-H2···C7(π) C10-H10A···Br1	2.51/172 3.0/150 3.17/171
II	0.5+x,y,0.5-z	5.221	-12.2	-4.4	-36.7	21.7	-31.6	stacking	
III	0.5-x,0.5+y,z	5.191	-7.8	-5.9	-40.5	32.9	-21.3	C5(sp^2)-H5···C1(π)	2.66/156
IV	x,0.5-y,-0.5+z	11.751	-2.9	-0.7	-8.3	5.8	-6.1	C11-H11B···Br1	3.27/130
V	0.5-x,-y,-0.5+z	11.948	-1.1	-0.2	-3.8	0.9	-4.2	C10-H10B···H10B-C10	2.31/126
	HxBr4								
I	0.5-x,-0.5+y,1.5-z	5.231	-18.1	-12.0	-47.2	37.8	-39.5	N1-H1···C2(π) C2(sp^2)-H2···C8(π) C9(sp^3)-H9B···C3(π)	2.70/163 2.91/157 2.89/146
II	0.5-x,1.5-y,1-z	5.527	-12.6	-5.8	-52.7	34.0	-37.1	C11A(sp^3)-H11A···C1(π)	2.97/139
III	0.5-x,0.5-y,1-z	6.464	-10.6	-5.2	-32.9	29.4	-19.3	C11A-H11B···Br1	3.18/139
IV	x,-1+y,z	6.168	-3.5	-3.2	-23.7	12.1	-18.4	Molecular stacking	
V	-0.5+x,1.5-y,-0.5+z	10.407	-6.4	-1.7	-14.4	12.6	-10.0	C9-H9B···Br1	3.11/112
VI	1-x,1-y,2-z	9.236	-0.6	-0.8	-8.0	3.0	-6.4	C3-H3···Br1	3.41/152
	HpF2								
I	0.5-x,0.5+y,z	5.274	-18.4	-11.7	-39.6	35.2	-34.6	N1-H1···C4(π) C9(sp^3)-H9B···C7(π)	2.72/164 2.81/144
II	-x,1-y,1-z	4.634	-18.7	-9.6	-56.6	51.5	-33.4	C9(sp^3)-H9A···C5(π) C13(sp^3)-H13B···C8(π) C13-H13B···N1	2.94/168 2.66/146 2.72/168

III	-x,-y,1-z	6.859	-5.7	-1.9	-23.3	12.5	-18.4	Molecular stacking	
IV	-0.5+x,0.5-y,1-z	6.187	-2.2	-1.9	-21.7	9.3	-16.4	C12-H12A···F1	2.63/144
V	0.5-x,0.5-y,0.5+z	9.826	-1.8	-1.0	-9.9	5.2	-7.4	C3-H3···H10B-C10	2.54/158/111
VI	x,1-y,0.5+z	9.870	-1.7	-0.5	-6.5	2.3	-6.4	C10-H10A···F1	2.70/146
	HpF4								
I	2-x,-y,1-z	5.461 1…2	-20.6	-13.8	-46.1	42.9	-37.6	N2-H2···C5(π) C(sp^3)22-H22A···C7(π) C22-H22B…F1 C26-H26A…F1	2.55/166 2.72/153 2.73/152 2.91/147
II	x,y,-1+z	5.196 1…2	-18.9	-12.3	-43.7	37.7	-37.2	N1-H1···C15(π) C9(sp^3)-H9A···C16(π) C2(sp^2)-H2A···C21(π)	2.62/170 2.88/152 2.97/160
III	x,y,z	5.093 1…2	-12.8	-5.5	-37.3	29.3	-26.3	C5(sp^2)-H5···C20(π) C13(sp^3)-H13B···C18(π)	2.80/147 2.85/138
IV	2-x,-y,1-z	6.380 1…1	-7.1	-3.0	-22.5	9.1	-23.5	Molecular stacking	
V	1-x,-y,1-z	5.347 1…2	-6.3	-4.5	-37.8	27.0	-21.6	C18(sp^2)-H18···C3(π) C26(sp^3)-H26B···C1(π)	2.99/162 2.96/133
VI	2-x,-y,2-z	7.602 2…2	-7.2	-1.3	-10.1	2.1	-16.5	Molecular stacking	
VII	1-x,-y,-z	6.132 1…1	-5.9	-2.7	-22.9	17.2	-14.2	Molecular stacking	
VIII	1-x,-y,1-z	6.821 2…2	-1.5	-1.1	-10.0	1.8	-10.8	Molecular stacking	
IX	1.5-x,-0.5+y,1.5-z	11.015 2…2	-4.2	-1.4	-9.2	6.3	-8.4	C10-H10B···F1	2.61/159
X	1.5-x,-0.5+y,0.5-z	11.008 1…1	-4.3	-1.7	-9.8	8.1	-7.7	C23-H23B···F2	2.76/152
	HpCL2								
I	2-x,-y,2-z	5.377	-18.1	-8.9	-67.5	56.5	-38.0	C12(sp^3)-H12B···C8(π) C10(sp^3)-H10A···C5(π) C12-H12B…N1	2.82/161 2.97/121 2.89/133
II	x,0.5-y,-0.5+z	5.549	-17.3	-10.6	-42.3	35.4	-34.8	N1-H1···C4(π) C9(sp^3)-H9B···C6(π)	2.64/164 2.73/152
III	2-x,-0.5+y,1.5-z	6.335	-5.1	-3.6	-30.9	20.2	-19.4	C12-H12A···Cl1	2.92/139
IV	-1+x,y,z	8.688	-3.6	-1.6	-15.7	8.5	-12.4	C9-H9A···Cl1	3.06/163
V	2-x,-y,1-z	8.039	-1.8	-0.3	-9.7	1.8	-10.0	Molecular stacking	
VI	-1+x,0.5-y,0.5+z	10.376	-3.4	-1.6	-13.7	9.0	-9.7	C10-H10B···Cl1	2.97/140

	HPCL3								
I	1-x,0.5+y,1.5-z	5.030	-25.0	-14.6	-48.5	39.2	-48.9	N1-H1···C5(π) C9-H9B···Cl1 C2(sp^2)-H2···C7(π)	2.67/167 3.00/126 2.96/159
II	1-x,-y,1-z	3.904	-13.4	-9.7	-71.2	53.3	-41.0	C13(sp^3)-H13B···C3(π)	2.89/139
III	1-x,1-y,1-z	6.312	-7.6	-2.3	-27.7	15.7	-21.9	Molecular stacking	
IV	x,0.5-y,-0.5+z	5.834	-0.7	-3.2	-29.9	16.8	-17.0	C13-H13A···N1 C5(sp^2)-H5···C2(π)	2.97/140 3.10/139
V	1+x,0.5-y,0.5+z	11.689	-3.4	-1.2	-10.7	6.5	-8.7	C11-H11B···Cl1	3.16/129
VI	2-x,-0.5+y,1.5-z	11.329	-1.4	-1.6	-12.1	9.4	-5.8	C9-H9A···H11B-C11 C10-H10A···H12B-C12	2.45/142/155 2.41/142/145
	HPCL4								
I	x,y,z	5.055 1…2	-19.5	-12.6	-51.2	40.1	-43.3	N1-H1···C15(π) C2(sp^2)-H2A···C21(π) C9(sp^3)-H9B···C16(π)	2.67/172 2.92/160 2.94/153
II	1-x,-y,1-z	5.742 1…2	-24.5	-16.3	-49.8	51.7	-38.8	N2-H2···C5(π) C22(sp^3)-H22B···C7(π)	2.55/161 2.69/153
III	x,y,-1+z	5.091 1…2	-15.1	-6.5	-44.5	33.4	-32.7	C13(sp^3)-H13A···C18(π) C22-H22A···Cl1 C26-H26B···Cl1	2.95/146 2.97/148 2.93/149
IV	-x,-y,1-z	5.250 1…2	-6.6	-5.3	-46.0	31.6	-26.3	C18(sp^2)-H18···C3(π) C26(sp^3)-H26A···C1(π) C25(sp^3)-H25B···C8(π)	3.07/166 3.03/128 3.10/151
V	1-x,-y,2-z	6.817 2…2	-7.1	-2.9	-20.6	7.8	-22.8	Molecular stacking	
VI	-x,-y,1-z	6.092 2…2	-7.6	-3.4	-30.5	19.9	-21.6	Molecular stacking	
VII	-x,-y,-z	6.661 1…1	-5.9	-2.9	-25.2	14.5	-19.5	C12-H12…Cl1 Molecular stacking	2.97/119
VIII	1-x,-y,1-z	7.574 1…1	-7.6	-1.3	-10.3	2.6	-16.7	Molecular stacking	
IX	0.5-x,0.5+y,0.5-z	11.367 1…1	-4.7	-1.8	-11.1	7.9	-9.7	C10-H10B···Cl1	2.90/146
X	0.5-x,-0.5+y,1.5-z	11.361 2…2	-3.9	-1.4	-10.8	6.5	-9.6	C23-23A···Cl2	2.91/151
	HPBr2								
I	1-x,-y,1-z	6.308	-17.9	-8.9	-68.5	56.5	-38.9	C12(sp^3)-H12B···C8(π) C10(sp^3)-H10B···C5(π)	2.81/161 2.98/121
II	x,0.5-y,-0.5+z	5.487	-15.5	-9.3	-39.0	32.1	-31.7	N1-H1···C4(π)	2.68/164

								C9(sp^3)-H9B···C6(π)	2.76/151
III	1-x,-0.5+y,0.5-z	6.654	-5.7	-3.3	-30.9	21.1	-18.8	C12-H12A···Br1 C13-H13A···Br1	3.05/137 3.24/114
IV	-1+x,y,z	8.786	-4.1	-1.5	-14.8	8.2	-12.1	C9-H9A···Br1	3.13/163
V	1+x,0.5-y,-0.5+z	10.395	-3.9	-1.4	-13.0	9.8	-8.4	C10-H10A···Br1	3.05/139
VI	1-x,-y,-z	8.815	-1.5	-0.2	-7.3	1.0	-8.1	Molecular stacking	
	HPBr3								
I	0.5-x,0.5-y,-0.5+z	4.869	-24.3	-13.3	-47.3	38.6	-46.3	N1-H1···C5(π) C10-H10B···Br1	2.66/171 3.11/156
II	0.5-x,0.5+y,z	5.652	-10.1	-3.1	-27.8	13.5	-27.4	Molecular stacking	
III	x,-y,-0.5+z	5.102	-8.8	-6.6	-44.7	35.4	-24.7	C5(sp^2)-H5···C1(π) C13(sp^3)-H13A···C8(π) C5-H5···N1	2.70/149 2.95/155 2.99/174
IV	1-x,y,1.5-z	12.507	-0.3	-0.8	-12.6	5.6	-8.1	C10-H10A···H10A-C10	2.53/136
V	1-x,-y,1-z	12.574	-2.5	-1.6	-14.2	11.1	-7.2	C11-H11A···H12A-C12	2.44/135/135
VI	-0.5+x,0.5-y,1-z	12.221	-4.4	-1.2	-9.4	8.0	-7.1	C11-H11B···Br1	3.12/135
	HPBr4								
I	1-x,1-y,1-z	6.063	-15.8	-6.9	-58.8	41.0	-40.5	C12(sp^3)-H12B···C7(π)	2.96/164
II	1-x,0.5+y,0.5-z	5.450	-14.8	-10.3	-40.9	30.9	-35.2	N1-H1···C2 C2(sp^2)-H2···C7(π)	2.73/158 2.891/129
III	x,1+y,z	6.206	-6.0	-4.2	-30.3	18.8	-21.7	Molecular stacking	
IV	1-x,-y,1-z	7.067	-6.5	-5.1	-22.2	19.3	-14.4	Molecular stacking	
V	-1+x,y,z	9.540	-4.3	-2.2	-15.0	9.1	-12.3	C11-H11B···Br1 C13-H13B···Br1	3.18/158 3.24/158
VI	-1+x,1+y,z	11.381	-4.3	-1.0	-8.1	5.1	-8.3	C9-H9B···Br1	3.05/130

Table S9: Isostructural similarity between different structures of Hx and Hp series of molecules.

Molecule 1	Molecule 2	Isostructurality	x	d (Å)	delta [a] (^{0})	delta [p] (^{0})
HxP	**HxF3**	**2D**	**11.0**	**0.11**	**4.3**	**10.0**
HxP	**HxF4_Form I**	**3D**	**4.5**	**0.23**	**1.9**	**3.9**
HxP	**HxCl3**	**1D**	**12.7**	**0.39**	**6.4**	**11.0**
HxP	**HxCl4**	**1D**	**9.8**	**0.05**	**3.7**	**9.1**
HxP	**HxBr4**	**1D**	**10.1**	**0.07**	**3.7**	**9.3**
HxF2	**HxBr3**	**1D**	**9.9**	**1.45**	**2.9**	**9.4**
HxF3	**HxF4_Form I**	**2D**	**11.4**	**0.14**	**4.6**	**10.4**

HxF3	**HxCl3**	**1D**	**12.1**	**0.48**	**6.5**	**10.2**
HxF3	**HxCl4**	**1D**	**4.5**	**0.07**	**1.8**	**4.1**
HxF3	**HxBr4**	**1D**	**4.1**	**0.03**	**1.7**	**3.7**
HxF4_Form I	**HxCl3**	**1D**	**11.9**	**0.31**	**5.6**	**10.5**
HxF4_Form I	**HxCl4**	**1D**	**10.7**	**0.05**	**4.4**	**9.7**
HxF4_Form I	**HxBr4**	**1D**	**10.9**	**0.09**	**4.4**	**10.0**
HxF4_Form II	**HxCl3**	**2D**	**11.0**	**0.44**	**4.6**	**9.8**
HxF4_Form II	**HxBr3**	**1D**	**6.9**	**0.18**	**3.1**	**6.1**
HxCl3	**HxCl4**	**1D**	**10.4**	**0.37**	**6.2**	**8.3**
HxCl3	**HxBr3**	**1D**	**10.9**	**0.05**	**4.8**	**9.7**
HxCl3	**HxBr4**	**1D**	**10.9**	**0.45**	**6.4**	**8.8**
HxCl4	**HxBr4**	**3D**	**1.2**	**0.14**	**0.6**	**1.0**
HpF4	**HpCl4**	**3D**	**4.0**	**0.16**	**1.6**	**3.6**
HpCl2	**HpBr2**	**3D**	**1.5**	**0.10**	**0.8**	**1.2**
HpCl3	**HpBr3**	**1D**	**4.8**	**0.07**	**1.9**	**4.3**

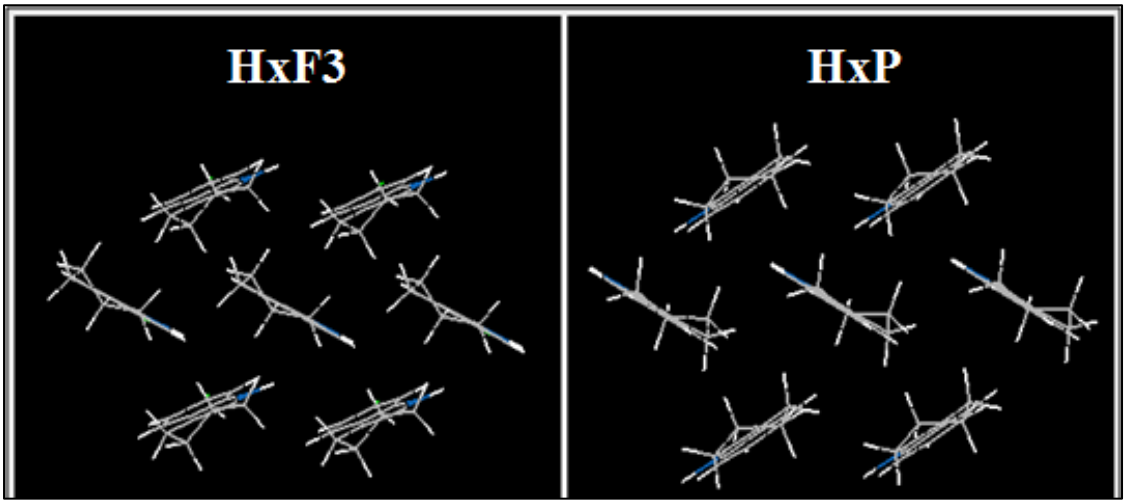

Figure 8a: 2D isostructurality between **HxP** and **HxF3**

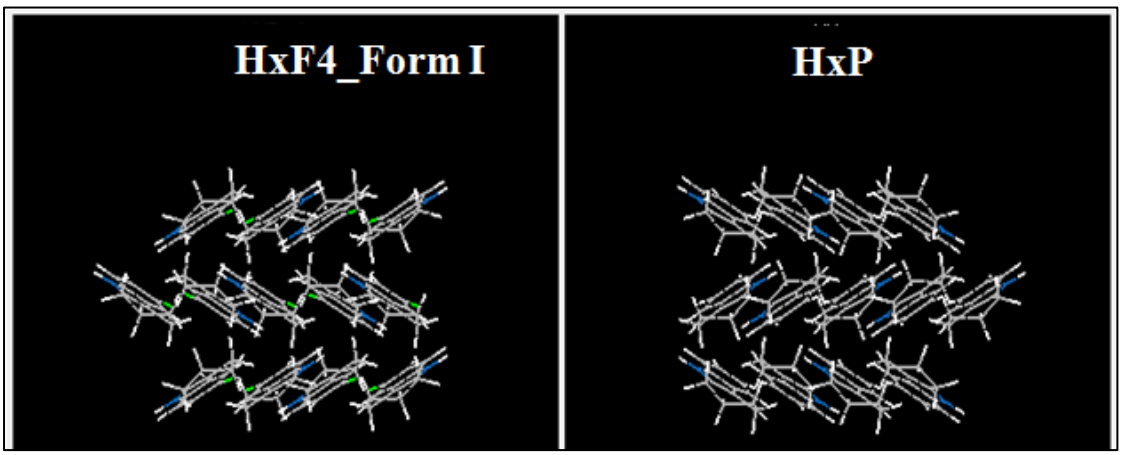

Figure 8b: 3D isostructurality between **HxP** and **HxF4_Form I**

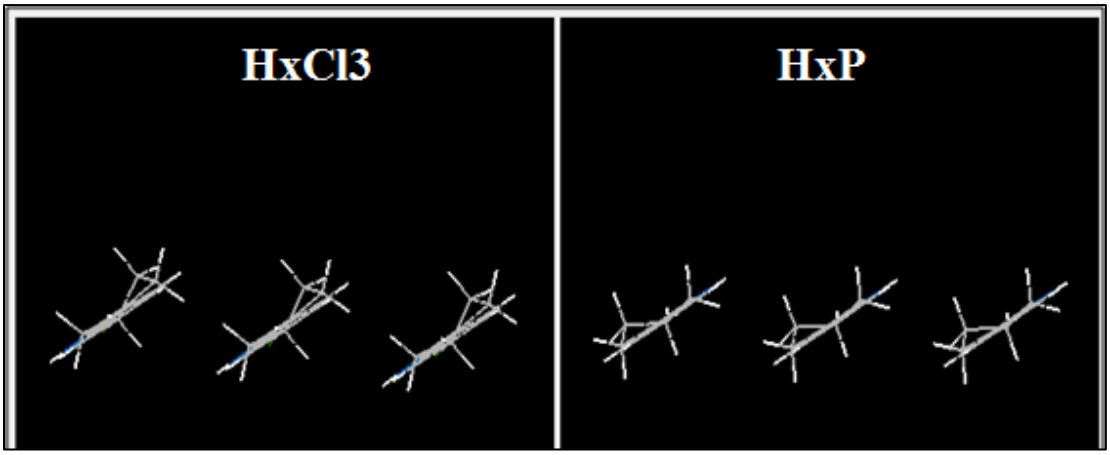

Figure 8c: 1D isostructurality between **HxP** and **HxCl3**

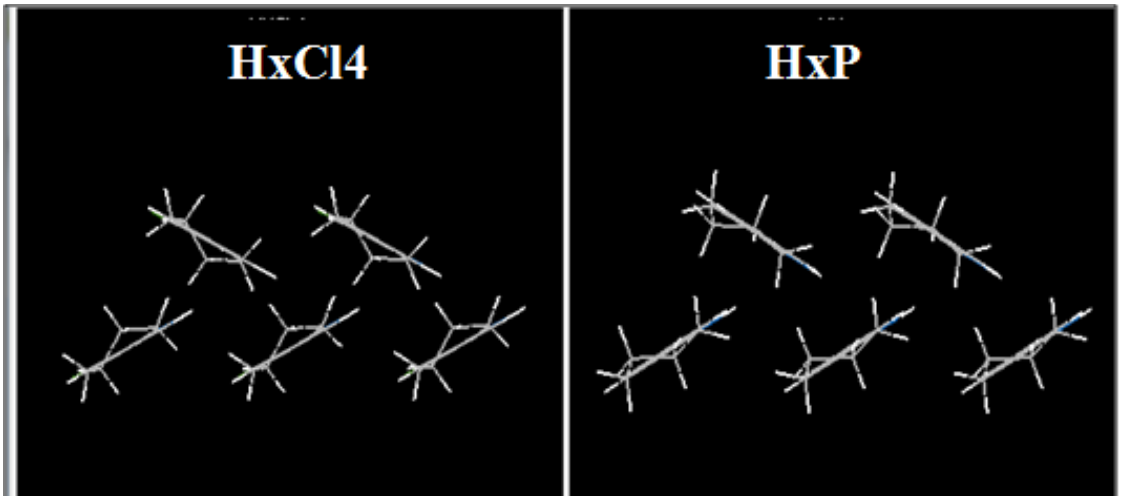

Figure 8d: 1D isostructurality between **HxP** and **HxCl4**

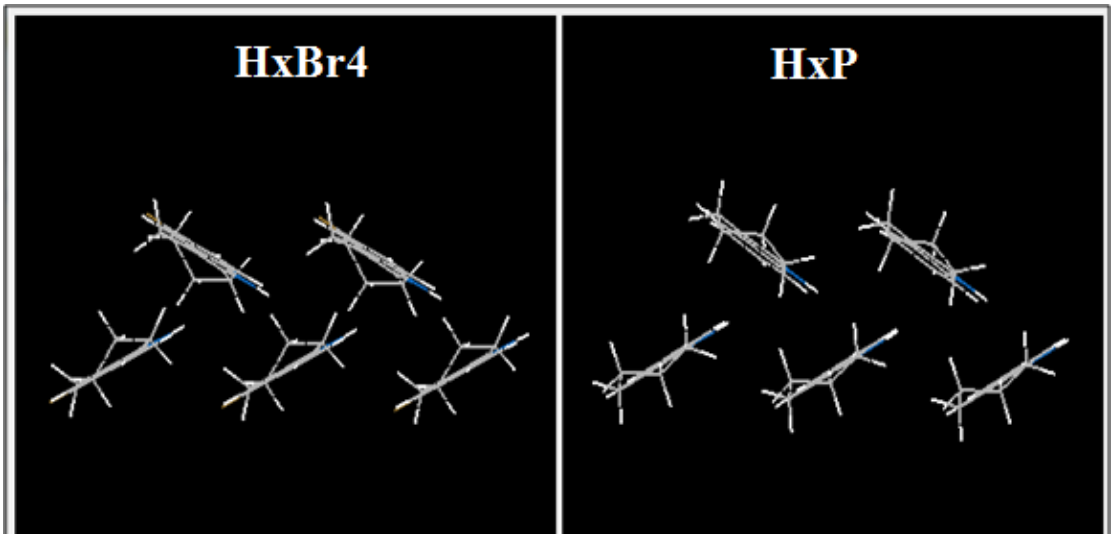

Figure 8e: 1D isostructurality between **HxP** and **HxBr4**

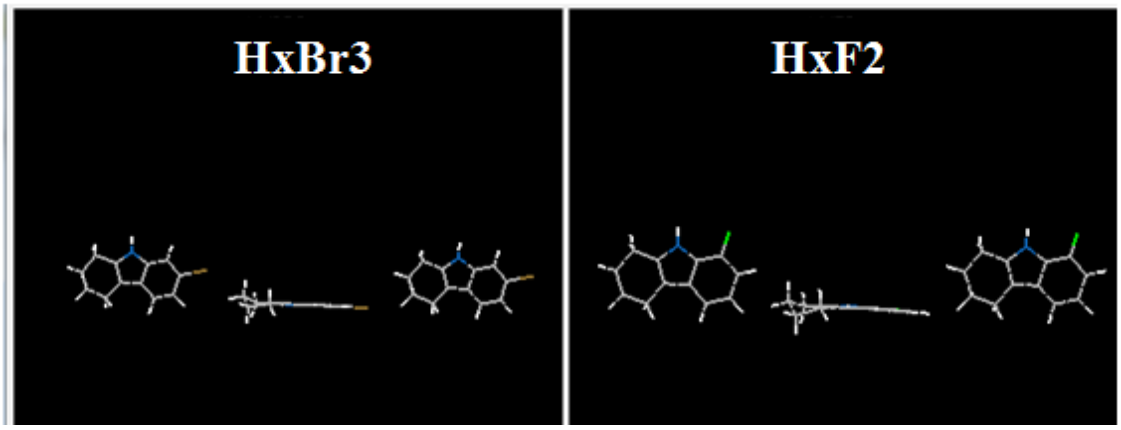

Figure 8f: 1D isostructurality between **HxF2** and **HxBr3**

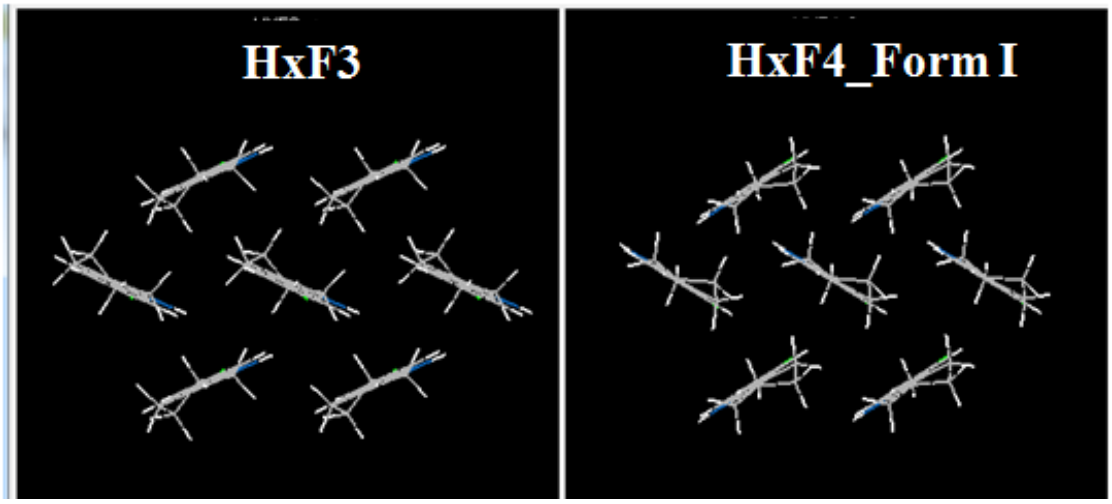

Figure 8g: 2D isostructurality between **HxF3** and **HxF4_Form I**

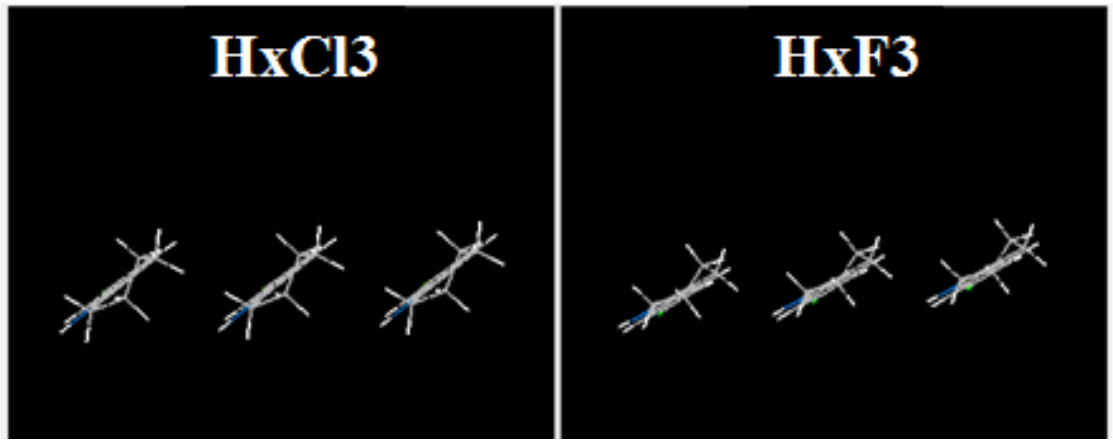

Figure 8h: 1D isostructurality between **HxF3** and **HxCl3**

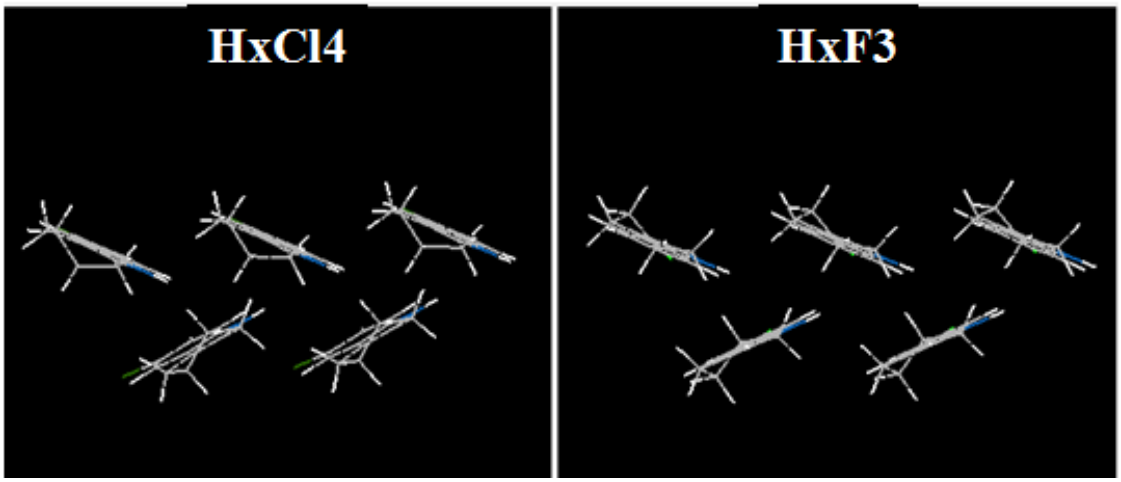

Figure 8i: 1D isostructurality between **HxF3** and **HxCl4**

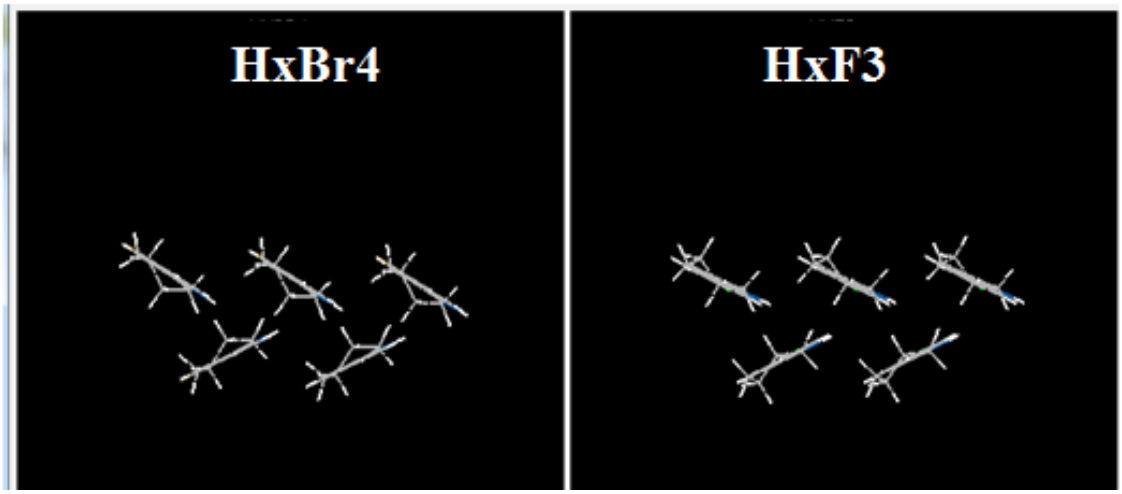

Figure 8j: 1D isostructurality between **HxF3** and **HxBr4**

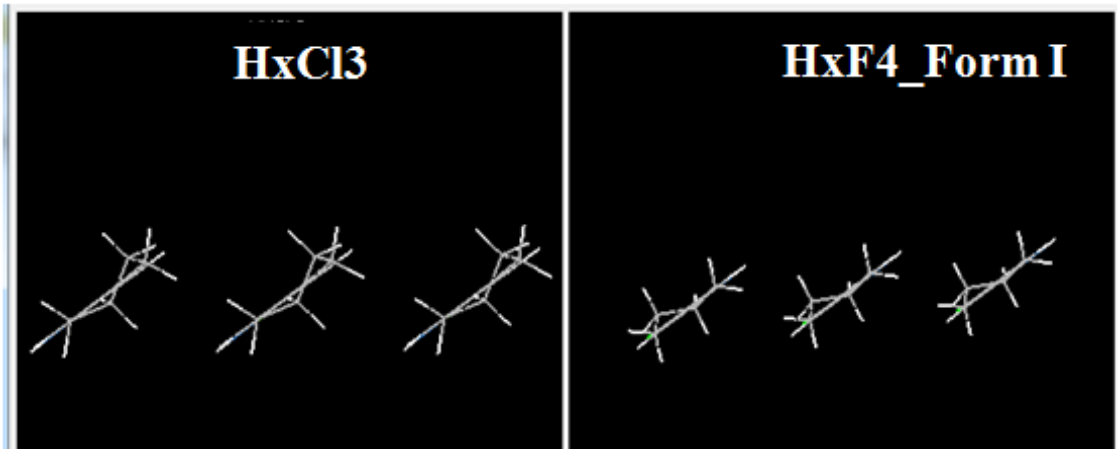

Figure 8k: 1D isostructurality between **HxF4_Form I** and **HxCl3**

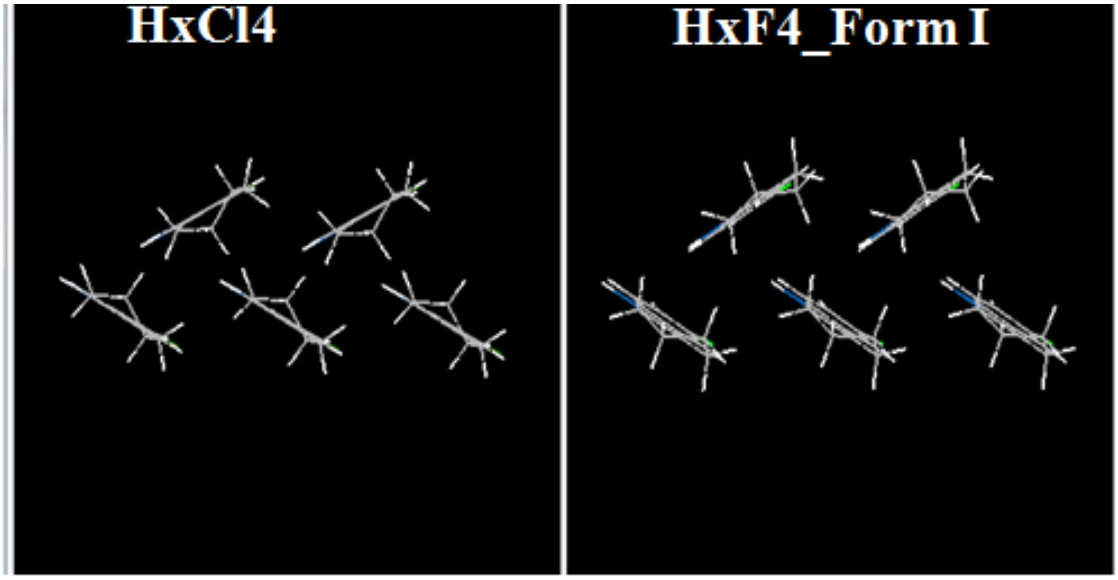

Figure 8l: 1D isostructurality between **HxF4_Form I** and **HxCl4**

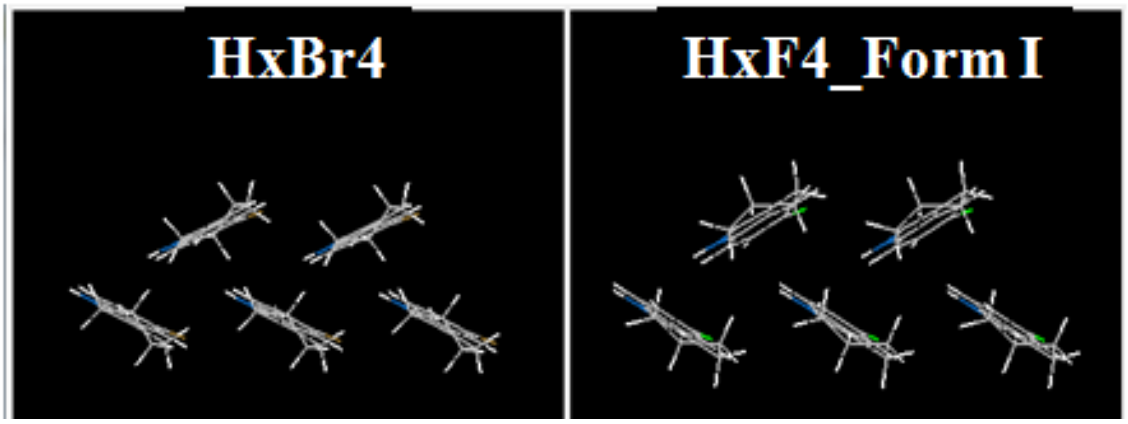

Figure 8m: 1D isostructurality between **HxF4_Form I** and **HxBr4**

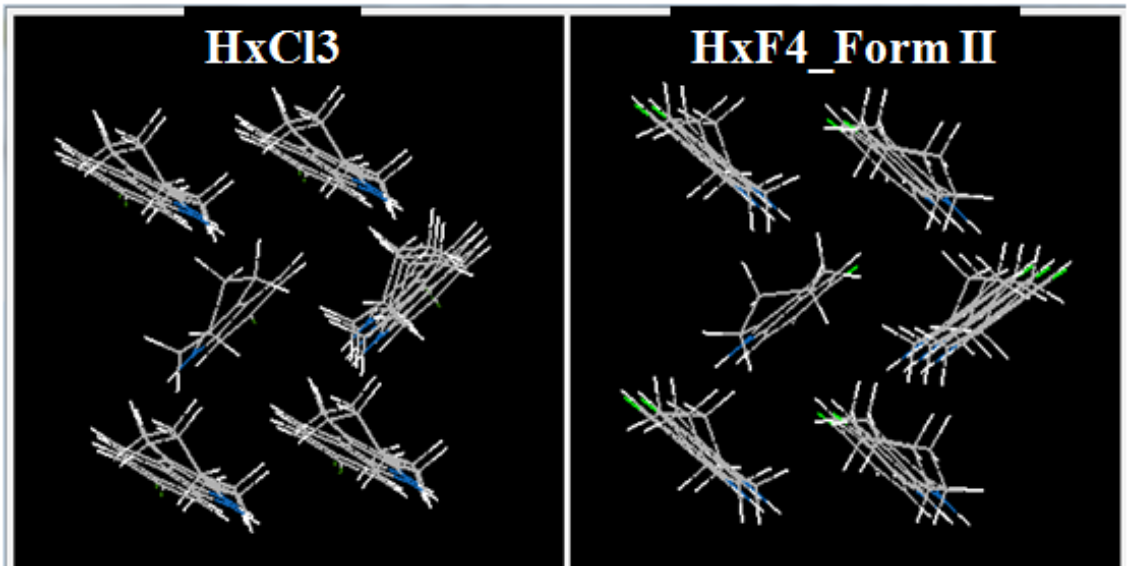

Figure 8n: 2D isostructurality between **HxF4_Form II** and **HxCl3**

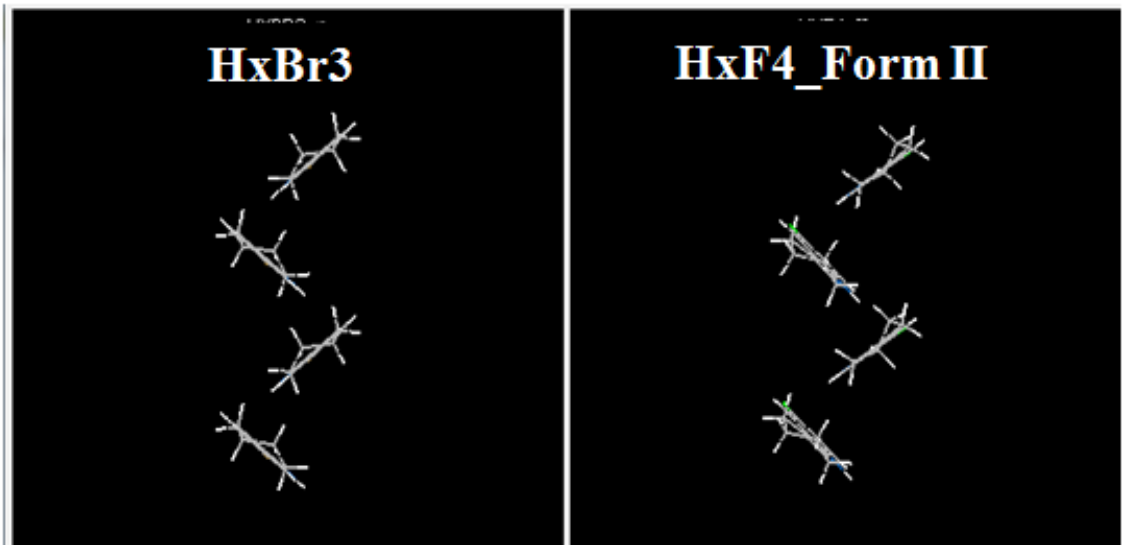

Figure 8o: 1D isostructurality between **HxF4_Form II** and **HxBr3**

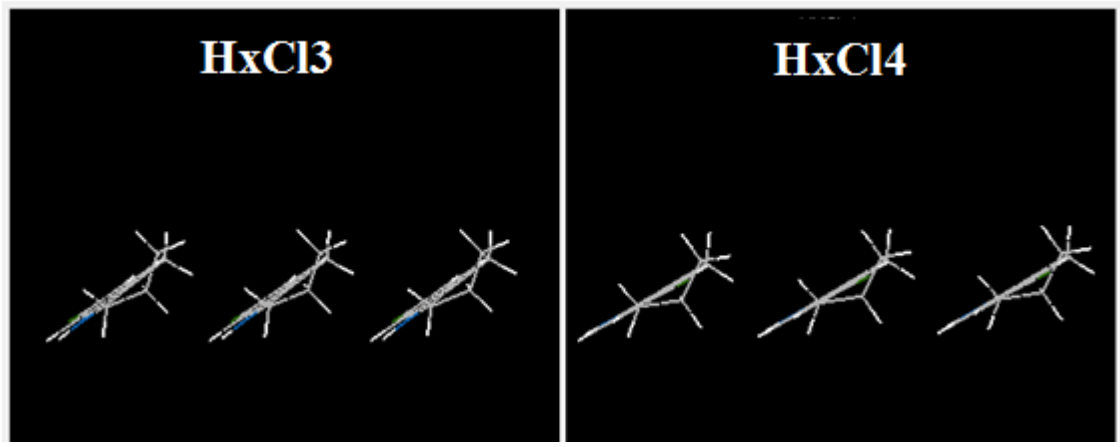

Figure 8p: 1D isostructurality between **HxCl3** and **HxCl4**

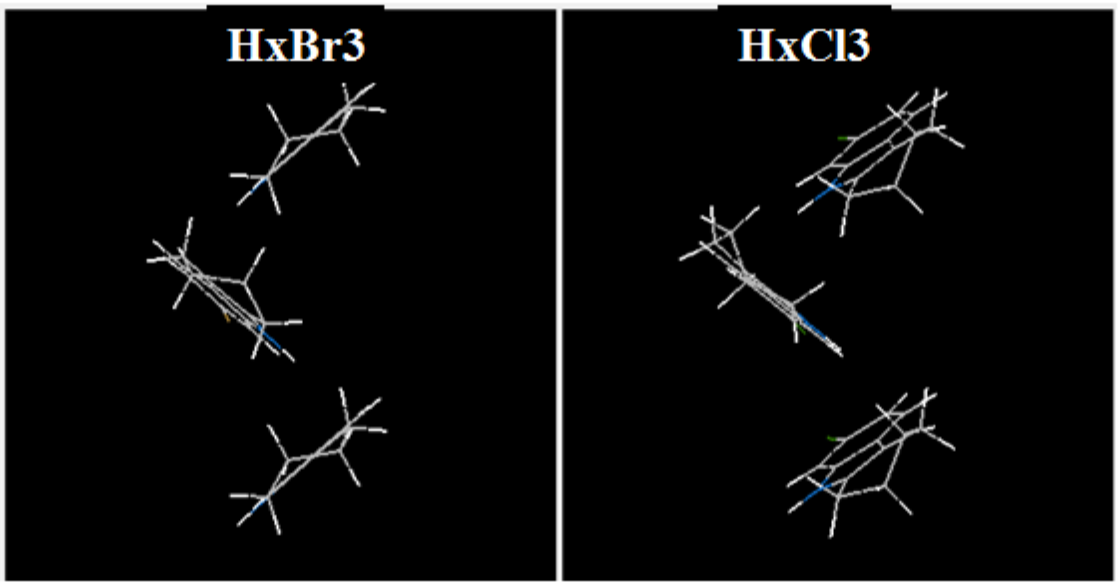

Figure 8q: 1D isostructurality between **HxCl3** and **HxBr3**

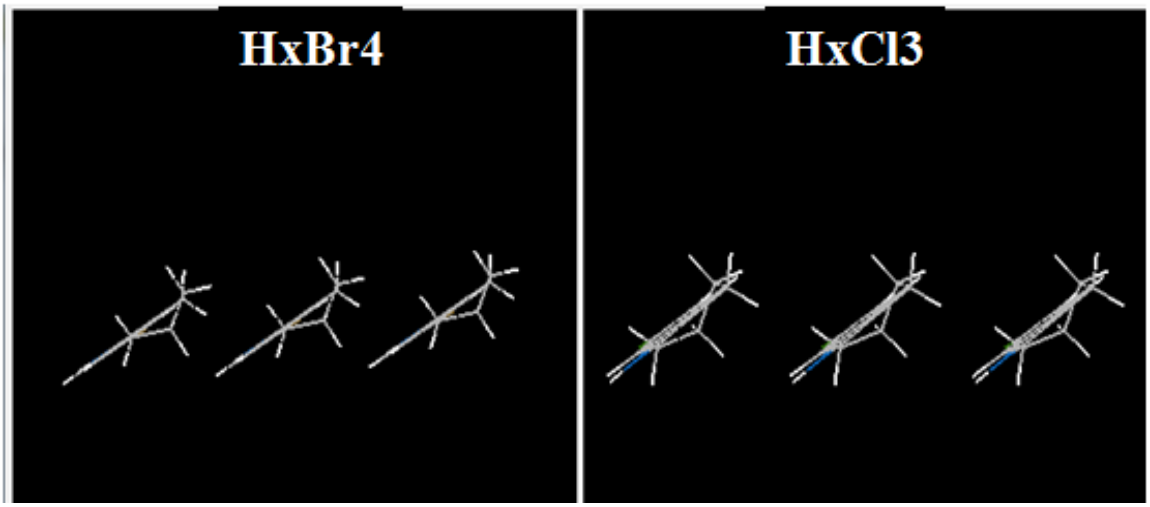

Figure 8r: 1D isostructurality between **HxCl3** and **HxBr4**

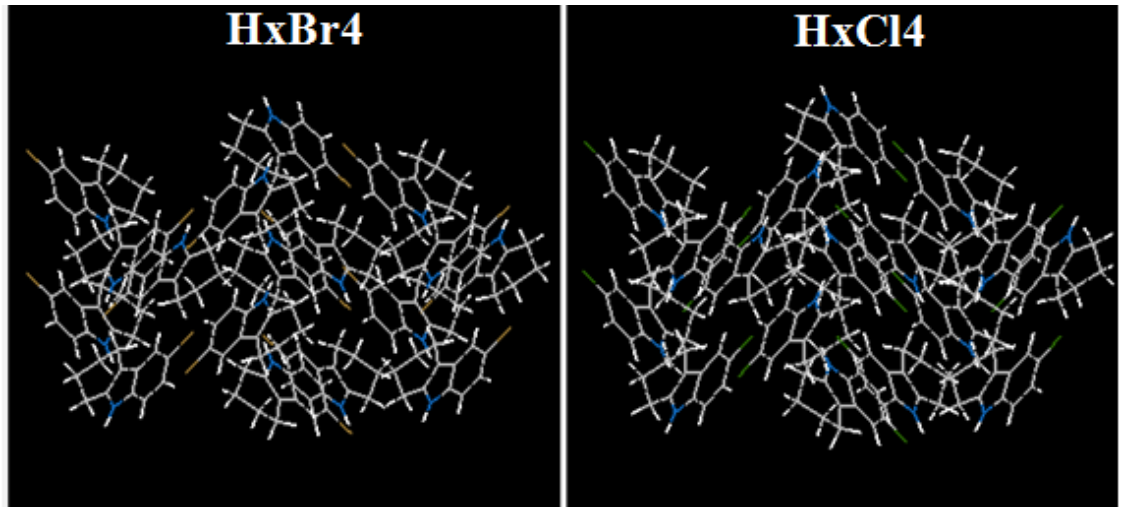

Figure 8s: 3D isostructurality between **HxCl4** and **HxBr4**

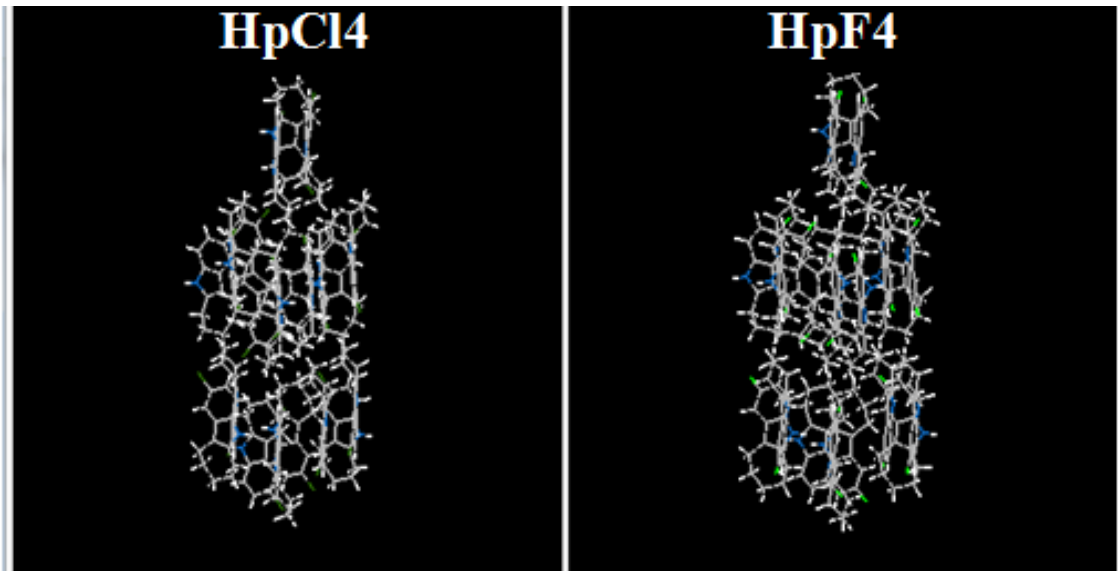

Figure 8t: 3D isostructurality between **HpF4** and **HpCl4**

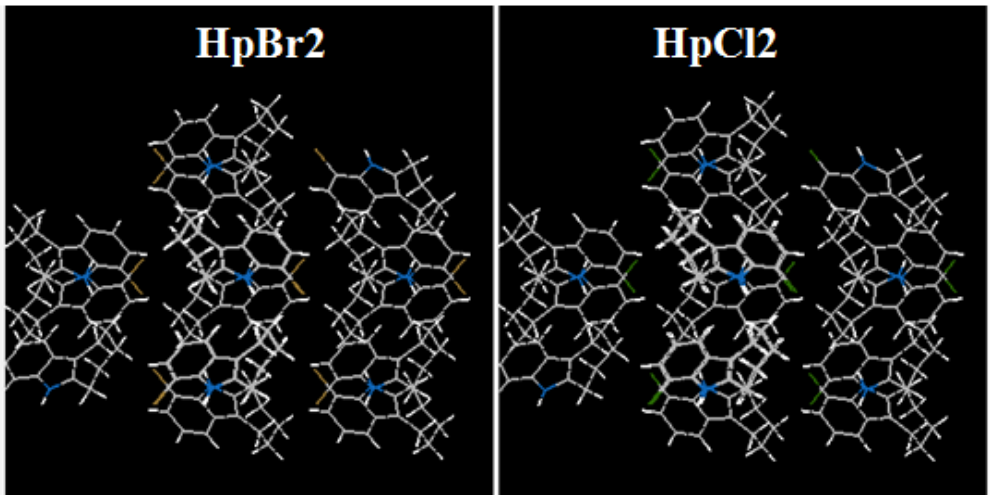

Figure 8u: 3D isostructurality between **HpCl2** and **HpBr2**

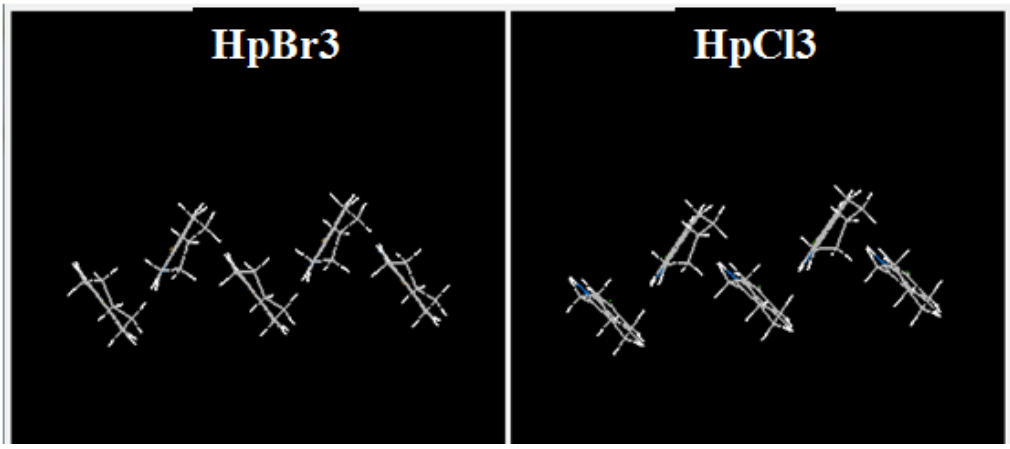

Figure 8v: 1D isostructurality between **HpCl3** and **HpBr3**

Table S10: Topological parameter obtained at N-H…C(π) bond critical point in different molecules.

	R_{ij}(Å)	**ρ (e/Å^3)**	**$\nabla^2\rho$ (e/Å^5)**	**|V|/G**
HxP	2.769	0.045	0.519	0.772
HxF2	2.578	0.065	0.784	0.745
HxF3	2.833	0.042	0.477	0.789
HxF4_I	2.812	0.051	0.629	0.764
HxF4_II_1	2.599	0.066	0.809	0.740
HxF4_II_2	2.562	0.062	0.724	0.754
HxCl2	2.733	0.048	0.509	0.761
HxCl3	2.904	0.061	0.728	0.739
HxCl4	2.717	0.050	0.592	0.768
HxBr3	2.598	0.064	0.752	0.745
HxBr4	2.751	0.048	0.558	0.773
HpF2	2.902	0.045	0.501	0.772

HpF4_1	2.839	0.055	0.651	0.759
HpF4_2	2.595	0.062	0.725	0.758
HpCl2	2.743	0.051	0.545	0.764
HpCl3	2.914	0.050	0.575	0.762
HpCl4_1	3.213	0.052	0.612	0.763
HpCl4_2	2.660	0.062	0.732	0.759
HpBr2	2.730	0.047	0.502	0.771
HpBr3	2.814	0.051	0.574	0.759
HpBr4	3.087	0.047	0.551	0.786