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**Supporting information for article:**

**Exploring concomitant/conformational dimorphism in a difluoro-substituted phosphoramidate derivative**

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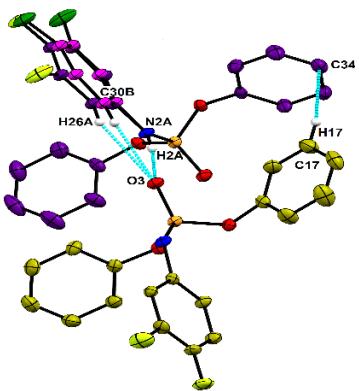
**Table S1** Crystallization summary

S.no.	Solvent	Method	Temperature (° C)	Form
1	Methanol	Slow	22-25	II
		Evaporation	4	II
2	Toluene	S.E.	22-25	I, II
			4	II
			-16	II
3	DCM-Hexane	S.E.	22-25	II
			4	I, II
			-16	II
4	Acetone	S.E.	22-25	II
			4	II
			-16	II
5	Acetonitrile	S.E.	22-25	II
6	Benzene	S.E.	4	II
7	Ethyl acetate	S.E.	4	II
8	Acetic Acid	S.E.	22-25	II
9	Methanol + Chloroform	Liquid diffusion	22-25	II
10	Trifluoro toluene	S.E.	22-25	II
11	Dioxane	S.E.	22-25	II
12	Cyclohexane	S.E.	22-25	II
			4	II
13	Ethyl acetate-Hexane	S.E.	22-25	II
14	CDCl <sub>3</sub>	S.E.	4	II
15	Ethanol	S.E.	22-25	II
16	THF	S.E.	22-25	II
17	Ethanol + Toluene	Liquid diffusion	22-25	II
18	Toluene + Hexane (1:3)	Liquid diffusion	22-25	II

19	Hexafluoro benzene	S.E.	4	II
20	Isopropanol	S.E.	22-25	II
21	Nitromethane	S.E.	22-25	II
			4	II
22	n-Pentane	S.E.	4	II
			-16	II
23	Methanol + Hexane	Vapor diffusion	22-25	II
			4	II
24	Chloroform	S.E.	4	II
			-16	II
25	Chloroform + Isooctane	S.E.	22-25	II
			4	II
26	Diisopropyl ether	S.E.	4	II
27	THF + n-Pentane	Vapor diffusion	22-25	II
28	Dioxane + n-Pentane	Vapor diffusion	22-25	II
29	Diisopropyl ether + Hexane	S.E.	4	II
			22-25	II
30	THF + Chloroform	Liquid diffusion	22-25	II

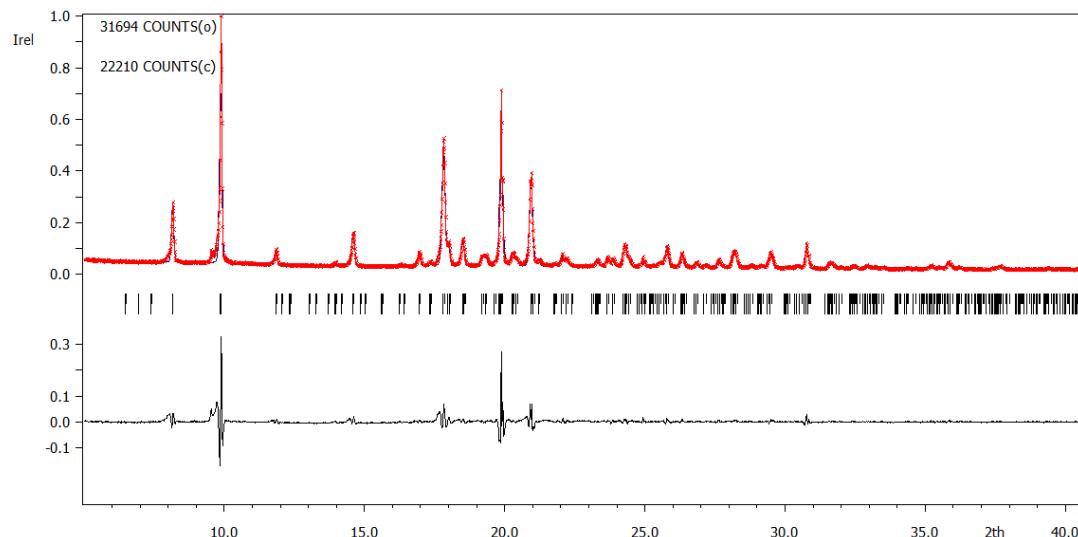
These are the library of solvent which have been tried for crystallization under varied conditions employing different methods repeatedly.

**Figure S1** ORTEP for disordered part in FORM II



### S1. Powder Xray diffraction-

The minimization of difference between the observed and calculated profiles is confirmed by low  $R_p$ ,  $R_{wp}$  value obtained after fitting the powder profile obtained from an experiment using program JANA 2006. Thereby, showing the convergence of data. Overlap of peaks for an organic molecule as such, in range of 5-40°, is sufficient to corroborate the existence of pure phase of Form II.



**Figure S2** Overlay of the simulated pattern (blue) over experimentally obtained powder pattern (red) of Form II to justify the existence of true phase [ $R_p=8.51$ ;  $wR_p=13.02$ ].

## S2. Single Crystal XRD-

**Table S2** Single Crystal Data Collection and Refinement

	(formI)	(formII)
Crystal data		
Chemical formula	$C_{18}H_{14}F_2NO_3P$	$C_{18}H_{14}F_2NO_3P$
$M_r$	361.27	361.27
Crystal system, space group	Monoclinic, $P2_1/c$	Orthorhombic, $Pca2_1$
Temperature (K)	100	100
$a, b, c$ (Å)	10.2037 (3), 9.1372 (3), 17.9981 (5)	35.0582 (8), 7.2554 (1), 13.3647 (3)
$\alpha, \beta, \gamma$ (°)	90, 92.260 (1), 90	90, 90, 90
$V$ (Å <sup>3</sup> )	1676.72 (9)	3399.46 (12)
$Z$	4	8

Radiation type	Mo $K\alpha$	Mo $K\alpha$
$\mu$ ( $\text{mm}^{-1}$ )	0.20	0.20
Crystal size (mm)	$0.24 \times 0.14 \times 0.10$	$0.32 \times 0.10 \times 0.08$
<b>Data collection</b>		
Diffractometer	Bruker <i>APEX-II</i> CCD	Bruker <i>APEX-II</i> CCD
Absorption correction	Multi-scan <i>SADABS</i>	Multi-scan <i>SADABS</i>
$T_{\min}, T_{\max}$	0.685, 0.746	0.683, 0.746
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	12986, 2935, 2724	38761, 9964, 7943
$R_{\text{int}}$	0.026	0.064
$(\sin \theta / \lambda)_{\max}$ ( $\text{\AA}^{-1}$ )	0.595	0.708
<b>Refinement</b>		
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.030, 0.080, 1.06	0.052, 0.115, 1.04
No. of reflections	2935	9964
No. of parameters	229	423
No. of restraints	0	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H-atom parameters constrained
$\Delta\rho_{\max}, \Delta\rho_{\min}$ ( $e \text{\AA}^{-3}$ )	0.27, -0.36	0.56, -0.39
Absolute structure	?	Refined as an inversion twin.
Absolute structure parameter	?	0.32 (11)

Computer programs: Bruker *APEX2*, Bruker *SAINT*, *SHELXS97* (Sheldrick 2008), *SHELXT* 2014/5 (Sheldrick, 2014), *SHELXL2018/3* (Sheldrick, 2018), *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008)"Bruker *SHELXTL*, *PLATON* (Spek, 2009) and *Mercury* (Macrae *et al.*, 2008), *WinGX* (Farrugia, 2014) and *PLATON*.

**Table S3** List of intra/intermolecular interactions

	<b>Form I</b>	D···A (Å)	H···A (Å)	D-H···A (°)
N1-H1A···O3	-x+1, -y, -z+2	2.8049(1)	1.78	176
C11-H11···O3	x, y-1, z	3.3832(1)	2.34	161
C16-H16···F1	x, -y-1/2, z+1/2	3.5841(1)	2.70	139
C18-H18···F2	-x+2, -y-1, -z+2	3.2700(1)	2.40	137
C12-H12···O3	-x+1, -y, -z+2	3.4748(1)	2.67	131
C18-H18···O2	-x+2, -y, -z+2	3.3759(1)	2.59	129
C6-H6···O3	x, y, z	3.232(0)	2.55	120
C8-H8···O1	x, y, z	3.178(0)	2.49	120
π···π	2-x, -y, 1-z	-	3.57	-
C16-H16...π(C9, C10,centroid)	x, -½-y, ½+z	3.6029(1)	2.69	170.7
	<b>Form II</b>			
N2-H2A···O3	x, y, z	2.7986(0)	1.78	172
C36-H36···F2	x, y-1, z+1	3.3913(1)	2.64	126
C18-H18···O6	x, y, z	3.6904(1)	2.76	144
C26A-H26A···O3	x, y, z	3.4111(1)	2.60	132
C30B-H30B···O3	x, y, z	3.2511(1)	2.35	140
N1-H1A ...O6	x, y+1, z	2.8194(0)	1.83	159
C26A-H26A···O5	x, y+1, z	3.3509(0)	2.45	140
C8-H8···O1	x, y+1, z	3.6384(0)	2.74	141
C8-H8···O6	x, y+1, z	3.3641(1)	2.54	132
C30B-H30B···O5	x, y+1, z	3.2602(1)	2.48	128
C30A-H30A···F3A	x, y-1, z	3.2917(0)	2.33	149
C26B-H26B···F3A	x, y-1, z	3.4137(0)	2.43	151
C12-H12···F1	x, y-1, z	3.3310(0)	2.38	146
C6-H6···F1	x, y-1, z	3.7719(1)	2.85	143
C32-H32···O3	x, y-1, z	3.3443(0)	2.36	150
C22-H22···F3A	-x+1, -y+1, z-1/2	3.5998(0)	2.71	139
C22-H22···F4B	-x+1, -y+1, z-1/2	3.2864(0)	2.40	138
C2-H2...O3	x, y, z	3.352(0)	2.648	122
C12-H12...O2	x, y, z	3.193(0)	2.473	123
C24-H24...O6	x, y, z	3.318(0)	2.603	123
C30A-H30A...O5	x, y, z	3.164(0)	2.481	120

C17-H17... π3(C34)	x, y, z	3.7407(0)	2.861	155
C6-H6...F4A	x, y, z-1	3.157(0)	2.492	119
C35-H35... π(centroid)	½-x, y, ½+z	-	2.67	155
C34-H34...π(C7, C8,C9/centroid)	½-x, -1+y, ½+z	-	2.554	161
C4-H4...π(C29A, C30A/centroid)	-x+1, -y+1, z+1/2	3.5449(1)	2.56	146

**Table S4** Pixel Table (in kJ/mol)

Motifs	Symmetry	D (Å)	E <sub>Coul</sub>	E <sub>Pol</sub>	E <sub>Disp</sub>	E <sub>Rep</sub>	E <sub>Tot</sub>	Possible interactions	Geometry (Å, °)
<b>P34F_Block (Form I)</b>									
I	1-x, -y, 2-z	6.138	-109.9	-42.6	-53.6	108.6	-97.5	N1-H1A…O3=P1	1.776, 176.2
II	2-x, -y, 2-z	5.522	-17.8	-7.8	-55.3	33.5	-47.4	C18-H18…O2-P1 C9-F1…C14(π)	2.592, 128.9 3.1491(1), 130.8
III	2-x, -1-y, 2-z	8.774	-10.4	-3.7	-24.3	16.2	-22.1	C18-H18…F2-C10 C10-F2…C9(π)	2.401, 136.5 3.1459(1)
IV	x, -1/2-y, -1/2+z	9.352	-3.6	-4.6	-27.8	18.4	-17.6	C16-H16…C9(π) C16-H16…C10(π) C16-H16…F1	2.6664(1), 168.8 2.8754(1), 159.2 2.698, 139.0
V	1-x, -1/2+y, 1.5-z	9.816	-4.9	-2.1	-18.8	8.2	-17.6	C4-H4…C11(π) C4-H4…C12(π)	3.0814(1), 145 2.9169(1), 138
VI	x, 1+y, z	9.137	-9.5	-3.9	-15.2	13.5	-15.2	C10-F2…O2-P1 C11-H11…O3=P1	3.1433(1) 2.4675(1), 162.0
VII	x, ½-y, ½+z	11.15	-6.1	-2.0	-13.7	8.0	-13.8	C15-H15…C6(π) C15-H15…C1(π)	2.8765(1), 159.8 3.0420(1), 146.3
<b>P34F_Needle (Form II)</b>									
I	x, -1+y, z	7.255	-11.3	-3.0	-19.4	9.1	-24.5	C12-H12…F1-C9 C8-H8…O2 C8-H8…O1	2.383, 145.6 2.736, 140.9
II	½-x, y, -1/2+z	10.15	-1.2	-1.3	-9.3	3.9	-7.8	C11-H11…H16-C16	3.820(1)
III	½-x, -1+y, 1/2+z	12.47	-1.6	-0.4	-5.7	0.9	-6.8	C16-H16…F1-C9	3.058, 141.6

IV	x, y, z	6.496	-63.3	-27.6	-50.2	71.9	-69.2	N2-H2A···O3=P1 C26A-H26A···O3=P1 C23-H23···C2(π1) C8-H8···O6=P2 C17-H17···C34(π6)	1.775,171.9 2.598,131.5  2.544,132.0  2.544,132.0
V	x, 1+y, z	6.569	-63.4	-26.8	-49.9	67.0	-73.1	N1A-H1A···O6=P2 C32-H32···O3=P1 C8-H8···O6=P2	1.832,159.4 2.364,150.2 2.544,132.0
VI	1-x, 1-y, - 1/2+z	9.048	-8.5	-5.5	-40.7	31.7	-22.9	C4-H4···C25A(π5) π 1···π4 (edge to edge)	2.910,166.6 3.501
VII	½-x, 1+y, - 1/2+z	9.664	-10.3	-6.2	-32.3	29.3	-19.5	C14-H14···C34/C33(π6- centroid) C34-H34···C7/C8/C9(π2)	2.794,143.0 2.554,161.5
VIII	½-x, y, - 1/2+z	9.615	-5.9	-2.9	-21.5	13.8	-16.5	C35-H35... π3	2.665, 155.3
IX	1-x, -y, - 1/2+z	10.24	-4.8	-1.4	-12.5	7.2	-11.6	C20-H20···C5(π1)	2.993,120.4
X	x, y, -1+z	8.893	-1.9	-1.6	-14.9	7.4	-11.0	C6-H6···F4A-C28A C28A-F4A···C11(π2) C27A-F3A···F2-C10	2.557,121.4 3.328,90.6,103.4 3.131,97.1,134.5
XI	x, 1+y, - 1+z	8.947	-2.8	-1.6	-13.6	7.9	-10.0	C10-F2···H29A-C29A C36-H36···F2-C10	2.838, 94.1 2.721,128.2
XII	x, -1+y, z	7.255	-11.4	-3.6	-19.5	12.9	-21.5	C30A-H30A···F3A-C27A C26A-H26A···O5	2.438,149.4 2.549,142.3
XIII	1-x, -y, - 1/2+z	10.19	-1.8	-1.7	-11.7	5.9	-9.4	C29A- H29A···C22/C21(π4/centr oid)	2.954, 156.9
XIV	1-x, 1-y, - 1/2+z	11.51	-2.8	-0.9	-7.5	3.7	-7.5	C22-H22···F4A-C28A C22-H22···F3A-C27A	2.651,131.5 2.811,141.0

Crystal	Atoms	Surface	Energies					
Interaction Energies (kJ/mol)								
R is the distance between molecular centroids (mean atomic position) in Å.								
Total energies, only reported for two benchmarked energy models, are the sum of the four energy components, scaled appropriately (see the scale factor table below)								
N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
1	x, y, z	9.14	B3LYP/6-31G(d,p)	-8.9	-2.7	-16.4	14.8	-16.6
2	-x, y+1/2, -z+1/2	9.82	B3LYP/6-31G(d,p)	-3.9	-0.9	-20.3	9.1	-16.9
2	x, -y+1/2, z+1/2	9.35	B3LYP/6-31G(d,p)	-2.2	-1.0	-29.1	18.7	-16.9
1	-x, -y, -z	6.14	B3LYP/6-31G(d,p)	-104.9	-25.8	-48.6	114.9	-101.4
1	-x, -y, -z	8.77	B3LYP/6-31G(d,p)	-8.2	-1.5	-30.5	17.8	-25.3
0	-x, -y, -z	9.17	B3LYP/6-31G(d,p)	5.1	-1.1	-8.2	2.5	-1.0
2	-x, y+1/2, -z+1/2	9.82	B3LYP/6-31G(d,p)	-0.9	-0.3	-5.2	0.5	-5.3
2	x, -y+1/2, z+1/2	11.16	B3LYP/6-31G(d,p)	-5.3	-0.7	-14.8	8.8	-13.6
1	-x, -y, -z	5.52	B3LYP/6-31G(d,p)	-14.6	-2.5	-61.2	38.3	-46.9
2	-x, y+1/2, -z+1/2	12.65	B3LYP/6-31G(d,p)	-0.8	-0.2	-3.5	0.3	-3.9
Scale factors for benchmarked energy models								
See Mackenzie et al. IUCrJ (2017)								
Energy Model			k_ele	k_pol	k_disp	k_rep		
CE-HF ... HF/3-21G electron densities			1.019	0.651	0.901	0.811		
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities			1.057	0.740	0.871	0.618		

**Figure S3** Energy decomposition via Energy Framework for Form I

Crystal	Atoms	Surface	Energies					
Interaction Energies (kJ/mol)								
R is the distance between molecular centroids (mean atomic position) in Å.								
N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
1	-	6.50	B3LYP/6-31G(d,p)	-57.8	-16.0	-50.0	75.6	-69.8
0	x, y, z	7.26	B3LYP/6-31G(d,p)	-9.6	-1.8	-22.1	10.8	-24.1
0	-	10.24	B3LYP/6-31G(d,p)	-3.9	-0.5	-12.8	7.8	-10.8
0	-	9.61	B3LYP/6-31G(d,p)	-4.7	-0.7	-22.6	12.7	-17.4
0	-x, -y, z+1/2	12.03	B3LYP/6-31G(d,p)	-0.3	-0.2	-3.2	0.2	-3.1
0	-x+1/2, y, z+1/2	10.15	B3LYP/6-31G(d,p)	-1.0	-0.5	-9.8	4.1	-7.5
0	-	9.05	B3LYP/6-31G(d,p)	-5.8	-1.0	-43.7	31.4	-25.5
0	-	8.89	B3LYP/6-31G(d,p)	-1.0	-0.7	-17.8	8.4	-11.9
0	-	8.95	B3LYP/6-31G(d,p)	-1.8	-0.7	-17.1	9.0	-11.7
0	-	6.57	B3LYP/6-31G(d,p)	-56.5	-16.3	-47.8	71.2	-69.5
0	-	9.66	B3LYP/6-31G(d,p)	-7.8	-1.0	-33.0	28.0	-20.5
0	-x+1/2, y, z+1/2	12.48	B3LYP/6-31G(d,p)	-1.2	-0.3	-6.9	1.3	-6.7
0	x, y, z	7.26	B3LYP/6-31G(d,p)	-9.8	-1.8	-22.0	14.4	-22.0
0	-x, -y, z+1/2	10.20	B3LYP/6-31G(d,p)	-1.5	-0.7	-12.4	6.8	-8.7
0	-x, -y, z+1/2	11.52	B3LYP/6-31G(d,p)	-2.2	-0.4	-8.6	4.7	-7.3
Scale factors for benchmarked energy models								
See Mackenzie et al. IUCrJ (2017)								
Energy Model			k_ele	k_pol	k_disp	k_rep		
CE-HF ... HF/3-21G electron densities			1.019	0.651	0.901	0.811		
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities			1.057	0.740	0.871	0.618		

**Figure S4** Energy decomposition via Energy Framework for Form II