Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information for

Supramolecular aggregation in sterically encumbered monoarylphosphates and their H-bonded adducts: Multigram synthesis of elusive 2,6-di-*tert*-butylphenyl phosphate

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Index

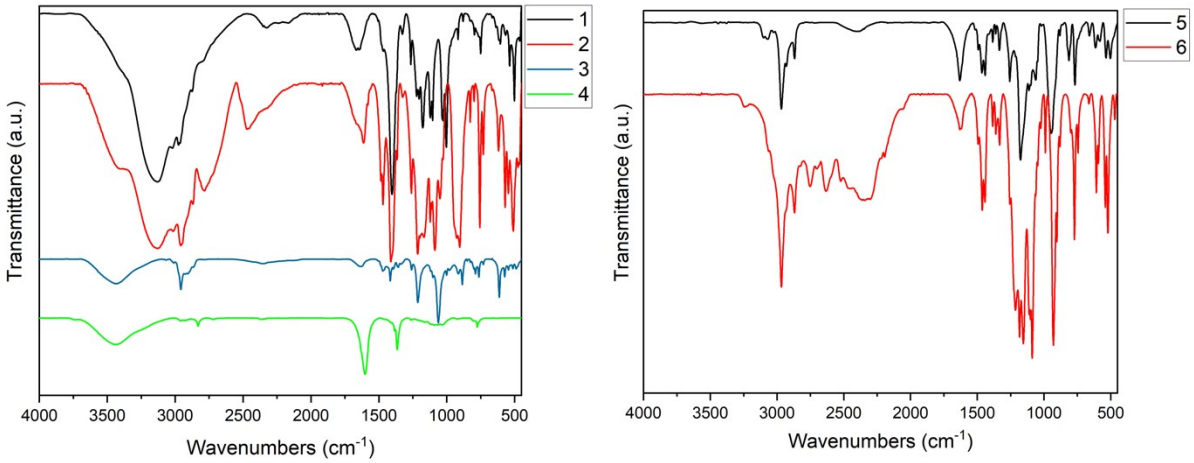


Fig. S1 FT-IR (as KBr disc) spectra of compounds **1-6.**

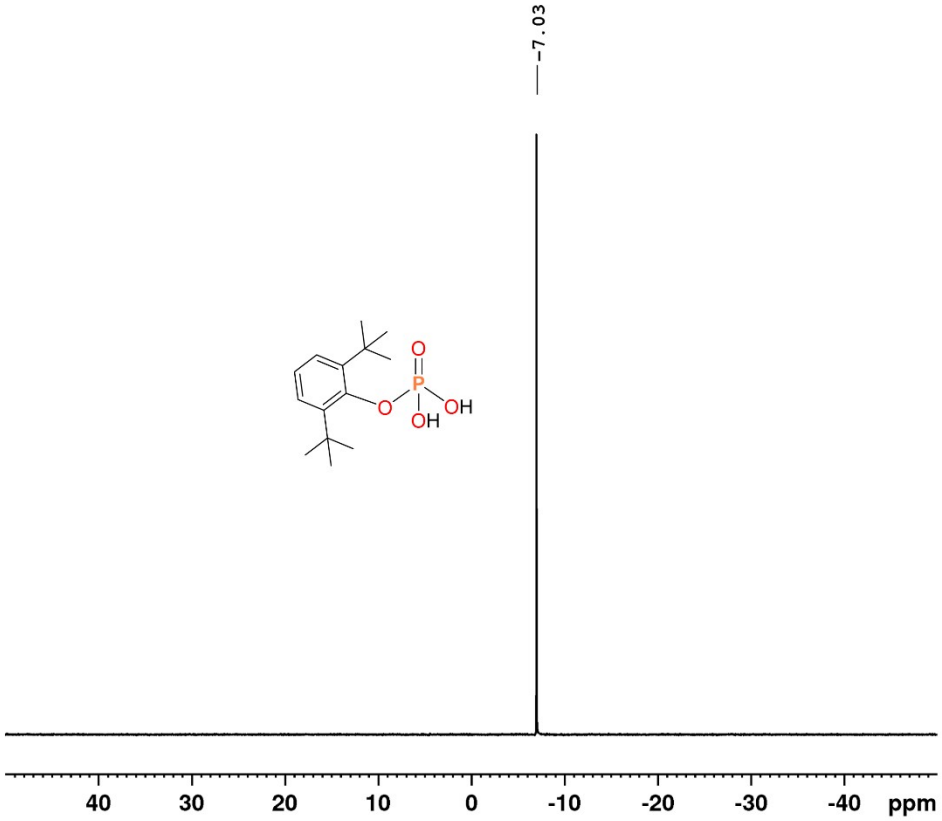


Fig. S2 ^{31}P NMR spectrum (DMSO-d_6 , 162 MHz) of compound **1.**

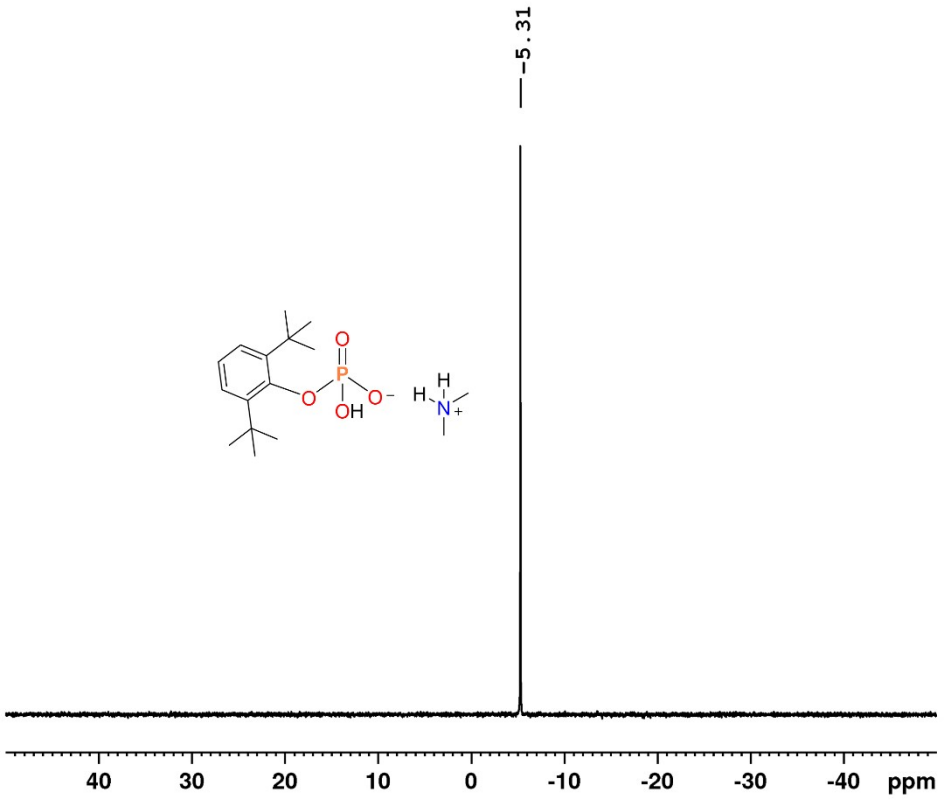


Fig. S3 ^{31}P NMR spectrum (CD_3OD, 162 MHz) of compound **2**.

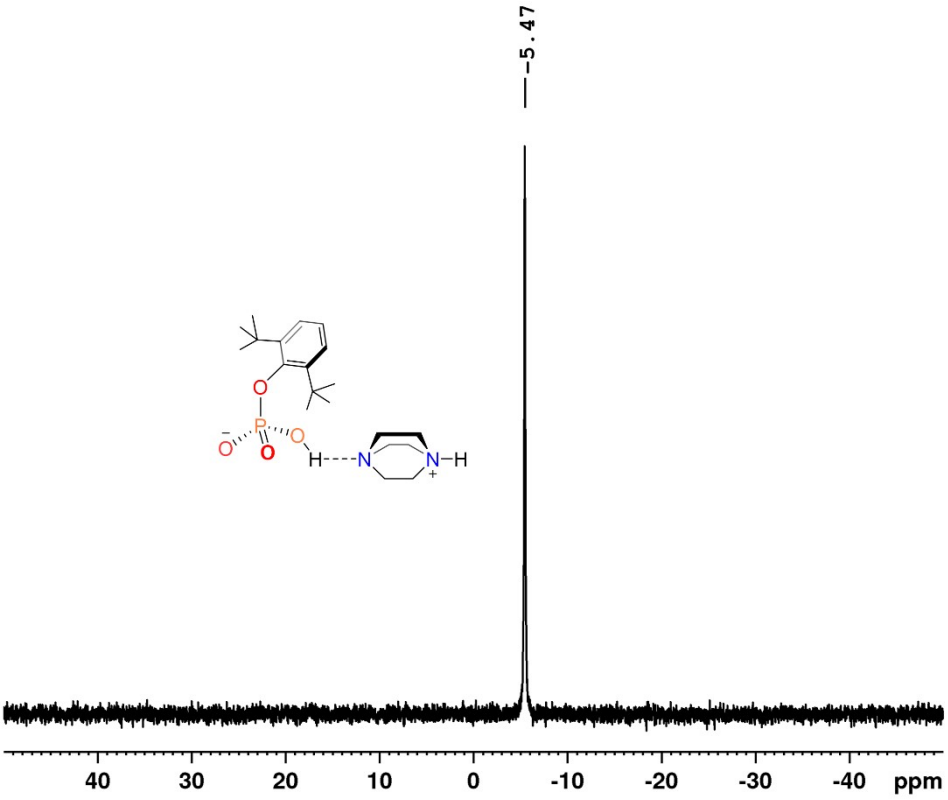


Fig. S4 ^{31}P NMR spectrum (CD_3OD, 162 MHz) of compound **3**.

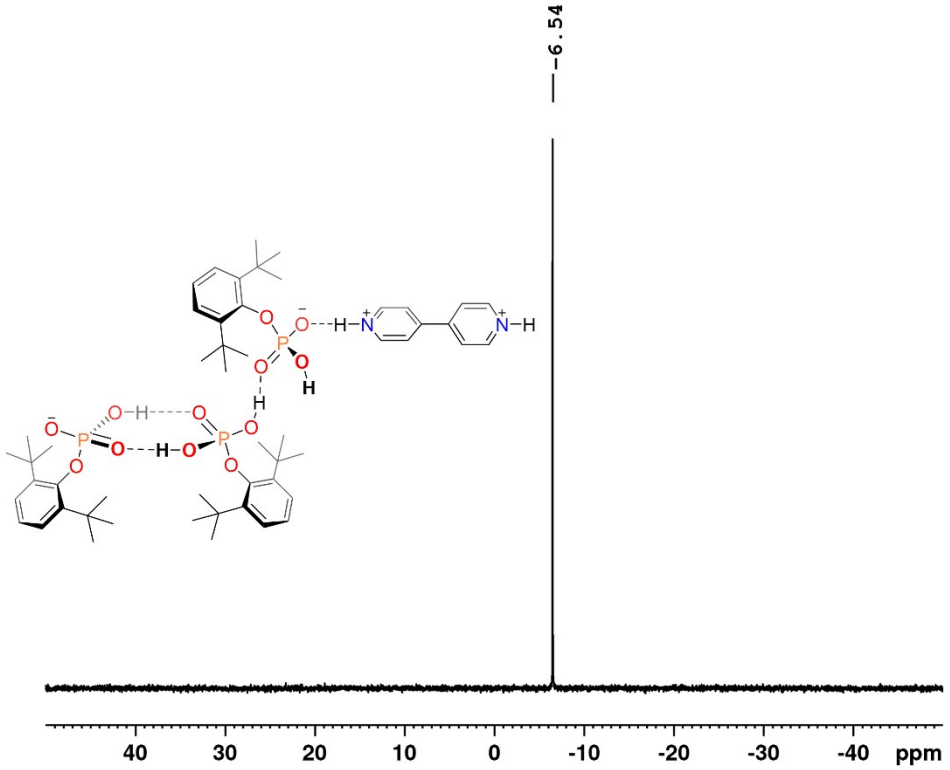


Fig. S5 ^{31}P NMR spectrum (CD_3OD, 162 MHz) of compound **4**.

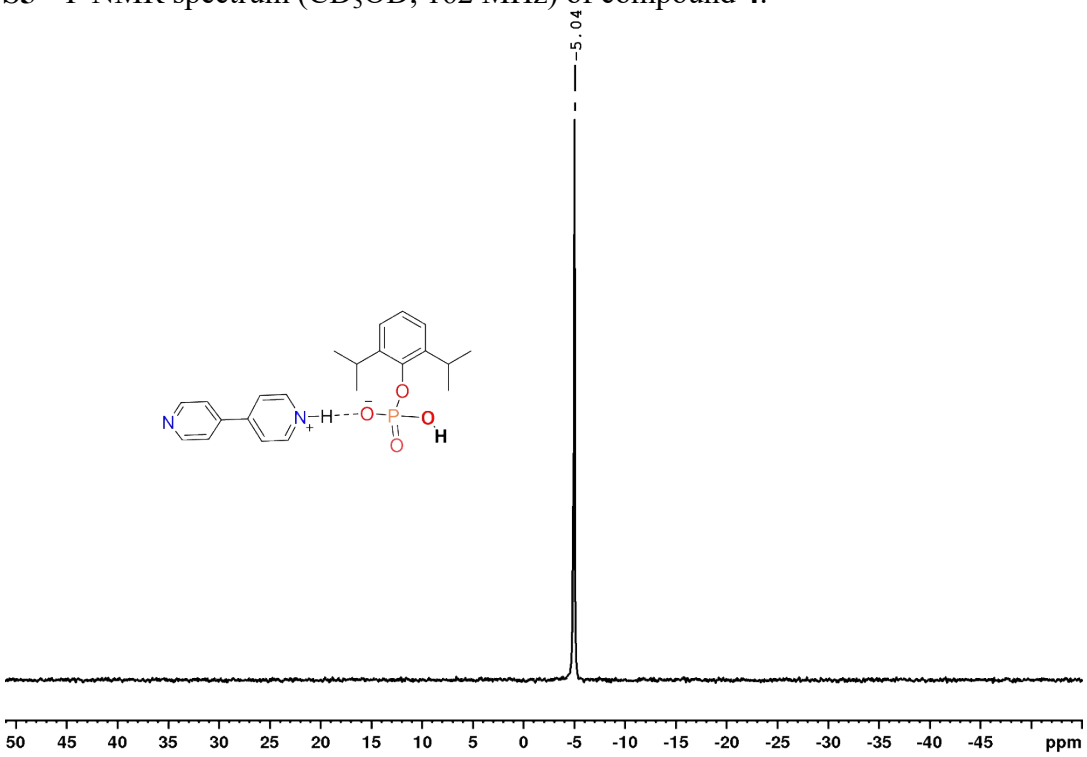


Fig. S6 ^{31}P NMR spectrum (CD_3OD, 202 MHz) of compound **5**.

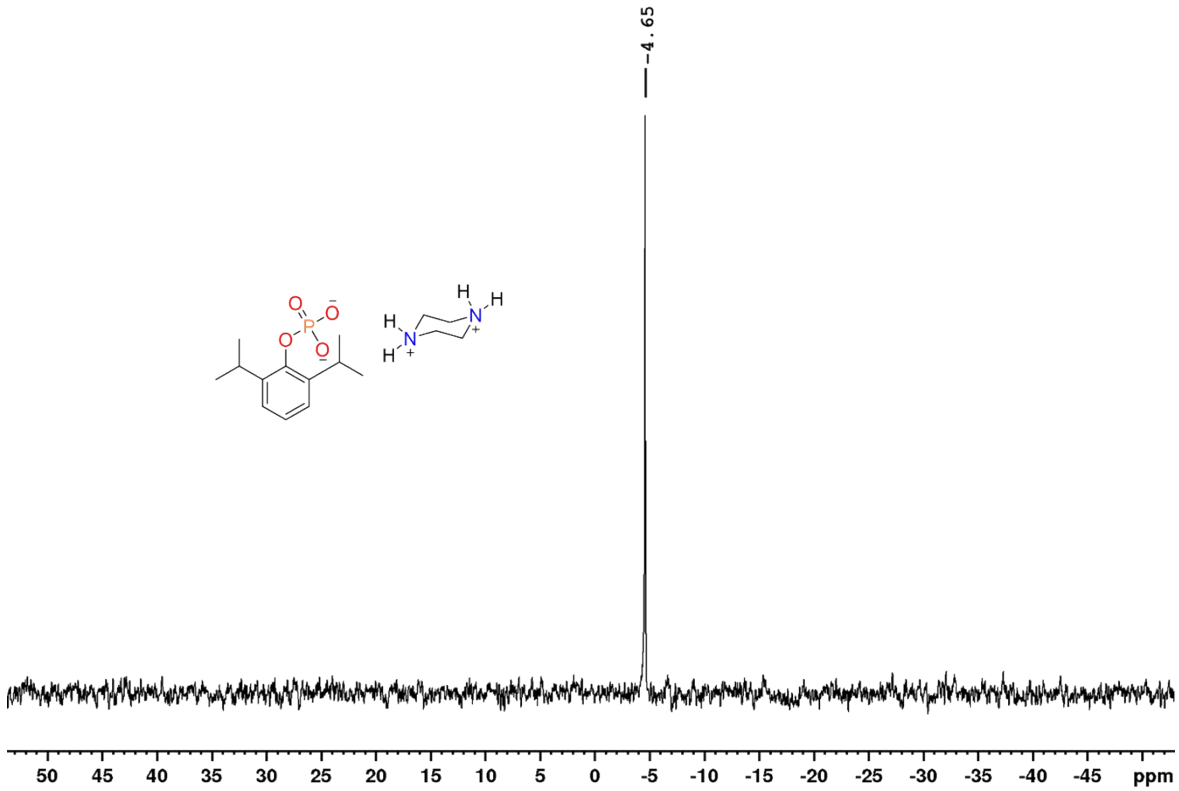


Fig. S7 ^{31}P NMR spectrum (CD_3OD, 202 MHz) of compound **6**.

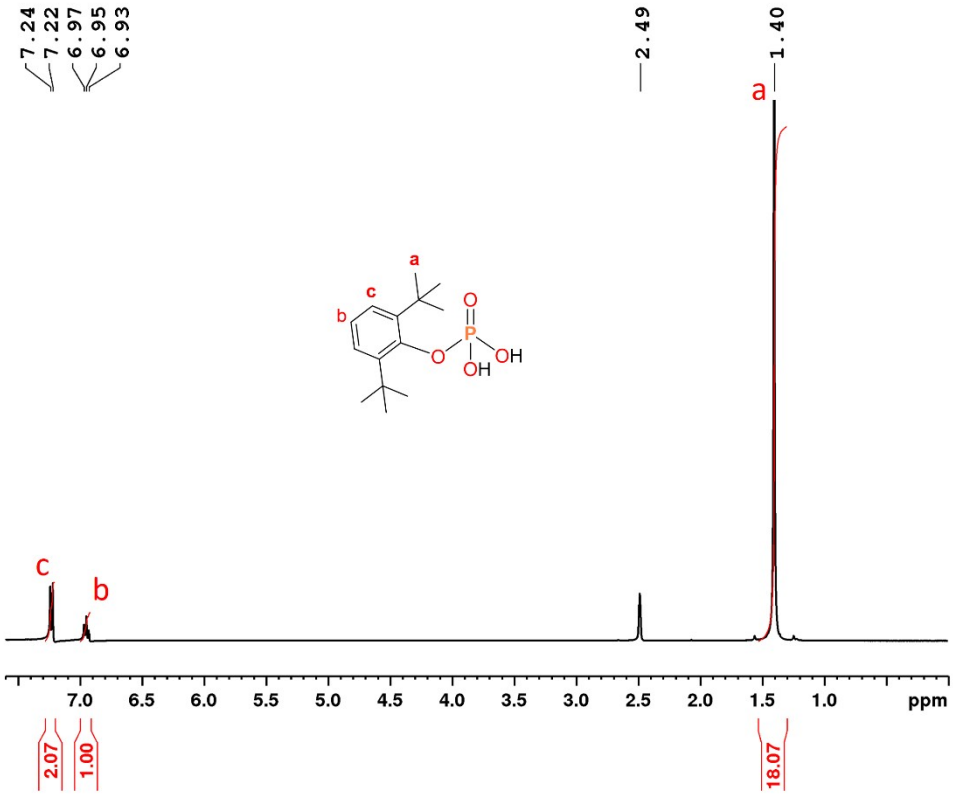


Fig. S8 ^{1}H NMR spectrum (DMSO-d6, 400 MHz) of compound **2**.

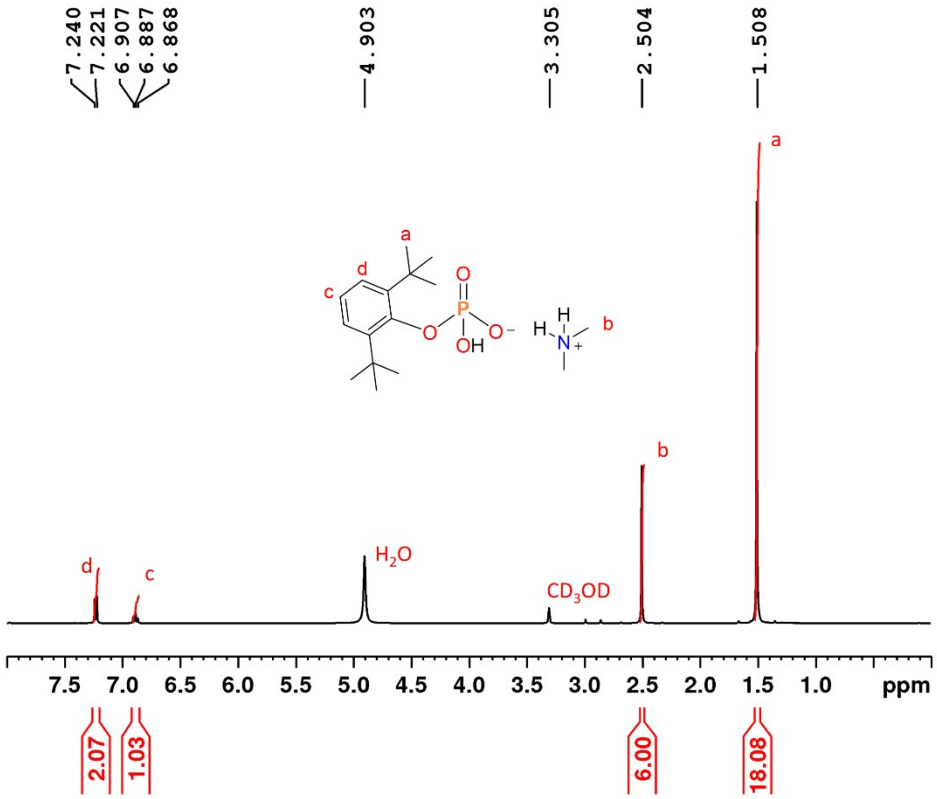


Fig. S9 ^{1}H NMR spectrum (CD_3OD, 400 MHz) of compound **2**.

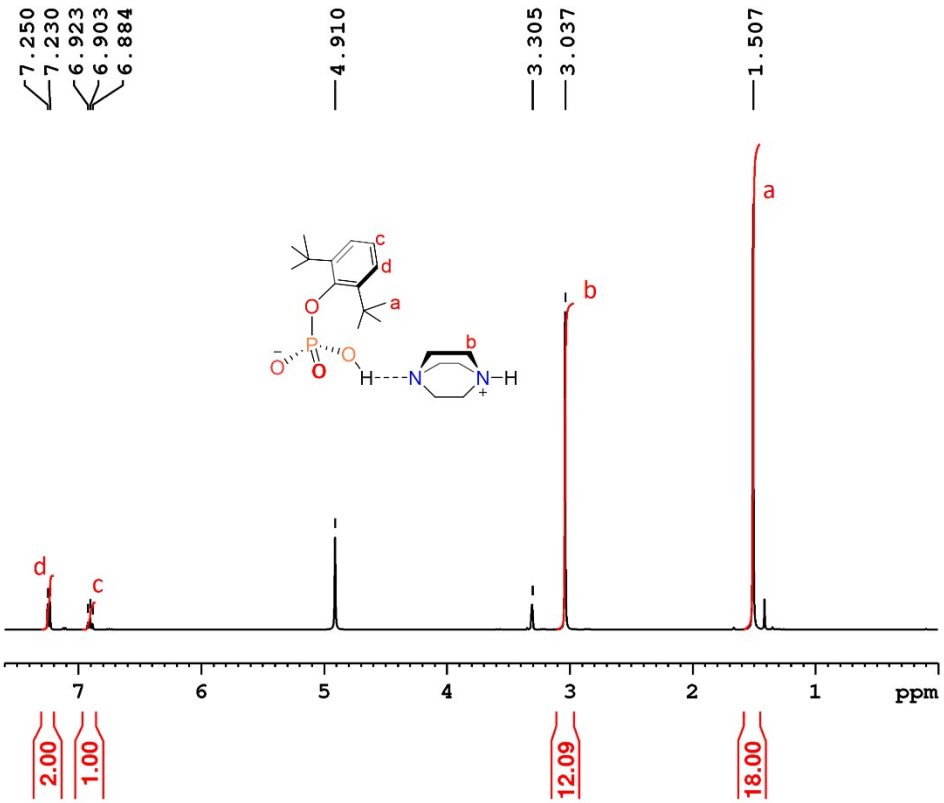


Fig. S10 ^{1}H NMR spectrum (CD_3OD, 400 MHz) of compound **3**.

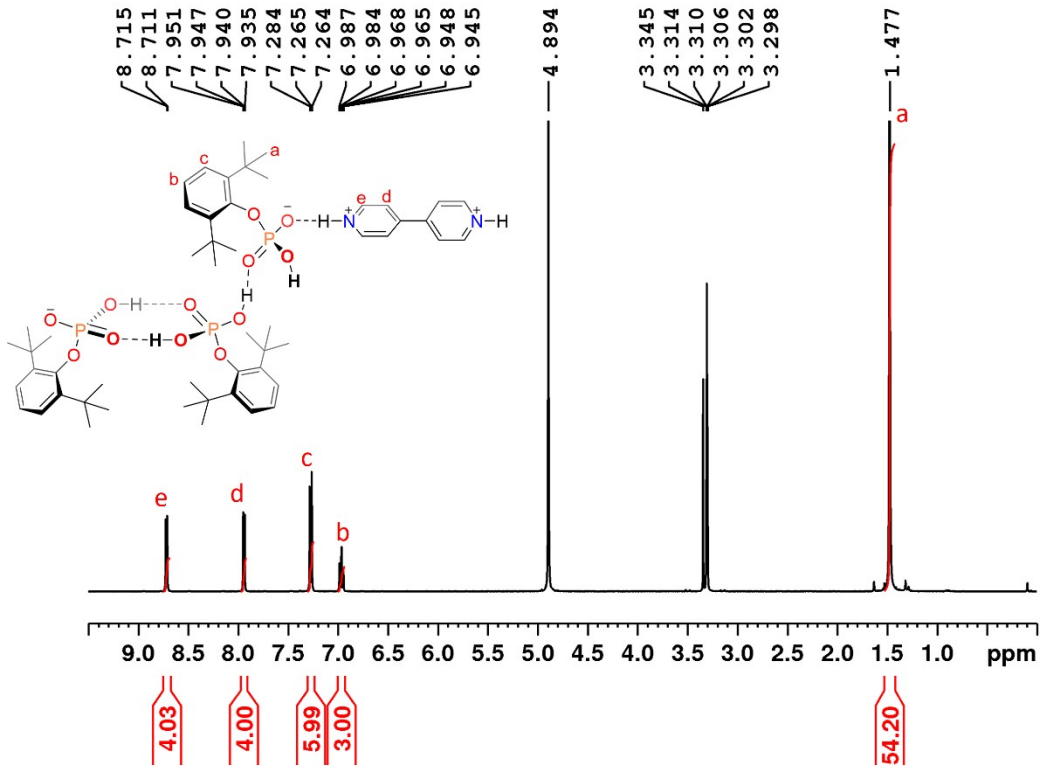


Fig. S11 ^{1}H NMR spectrum (CD_3OD, 400 MHz) of compound **4**.

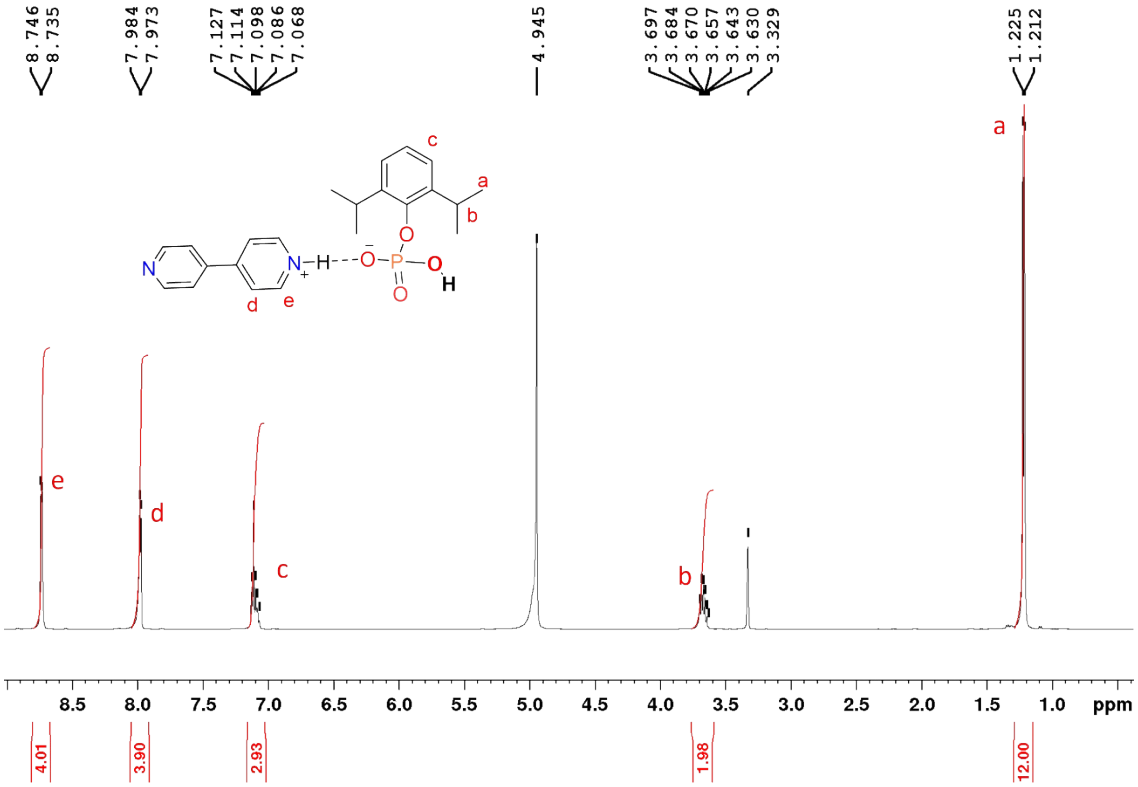


Fig. S12 ^{1}H NMR spectrum (CD_3OD, 500 MHz) of compound **5**.

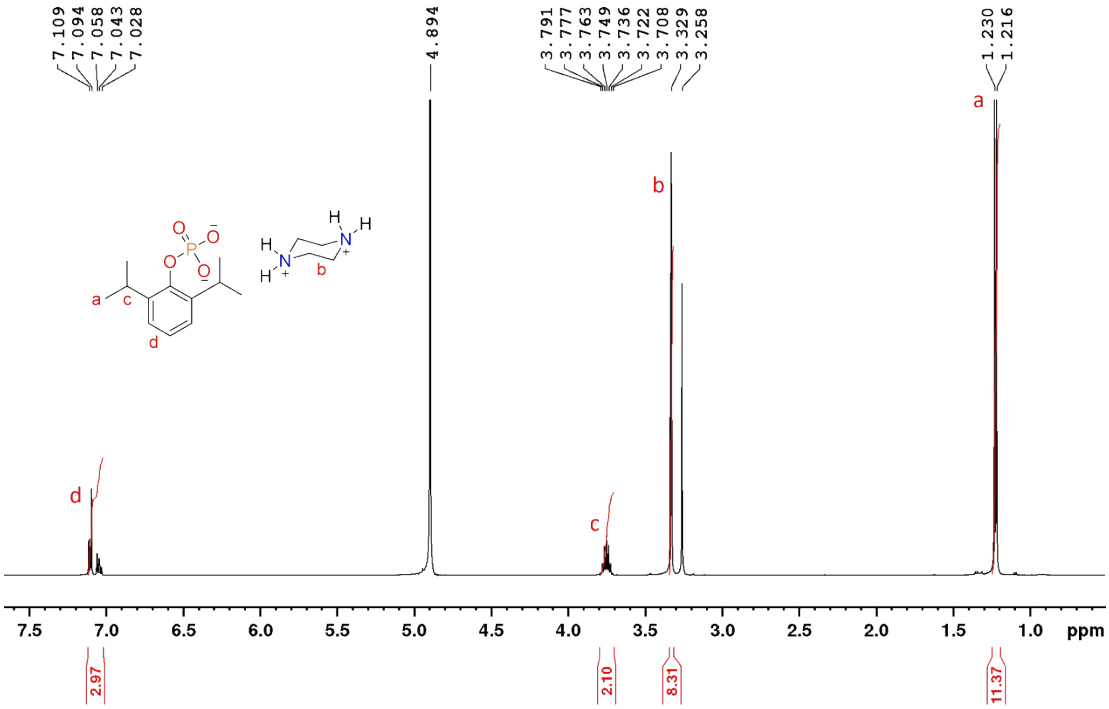


Fig. S13 ^{1}H NMR spectrum (CD_3OD, 500 MHz) of compound **6**.

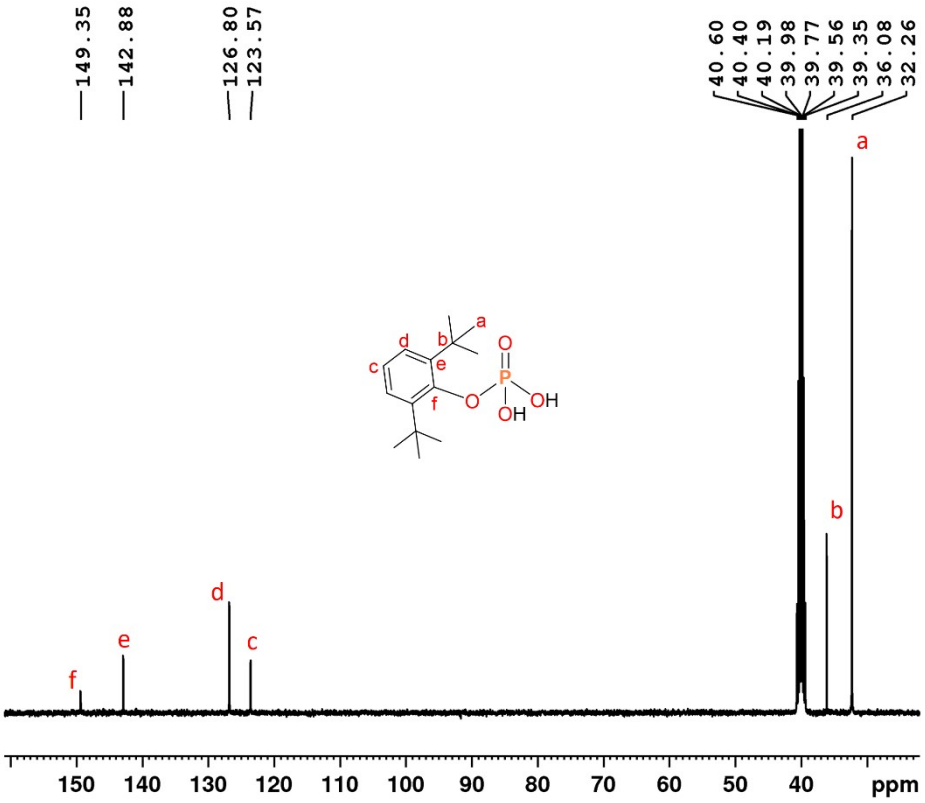


Fig. S14 ^{13}C NMR spectrum (DMSO-d_6, 100 MHz) of compound **1**.

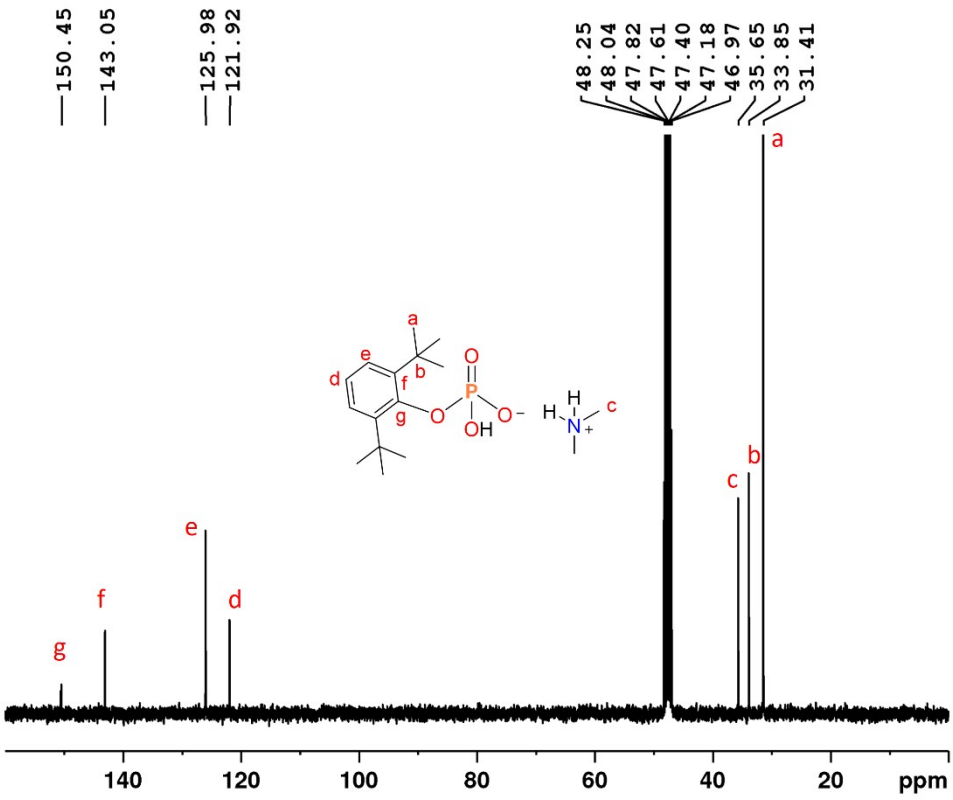


Fig. S15 ^{13}C NMR spectrum (CD_3OD, 100 MHz) of compound **2**.

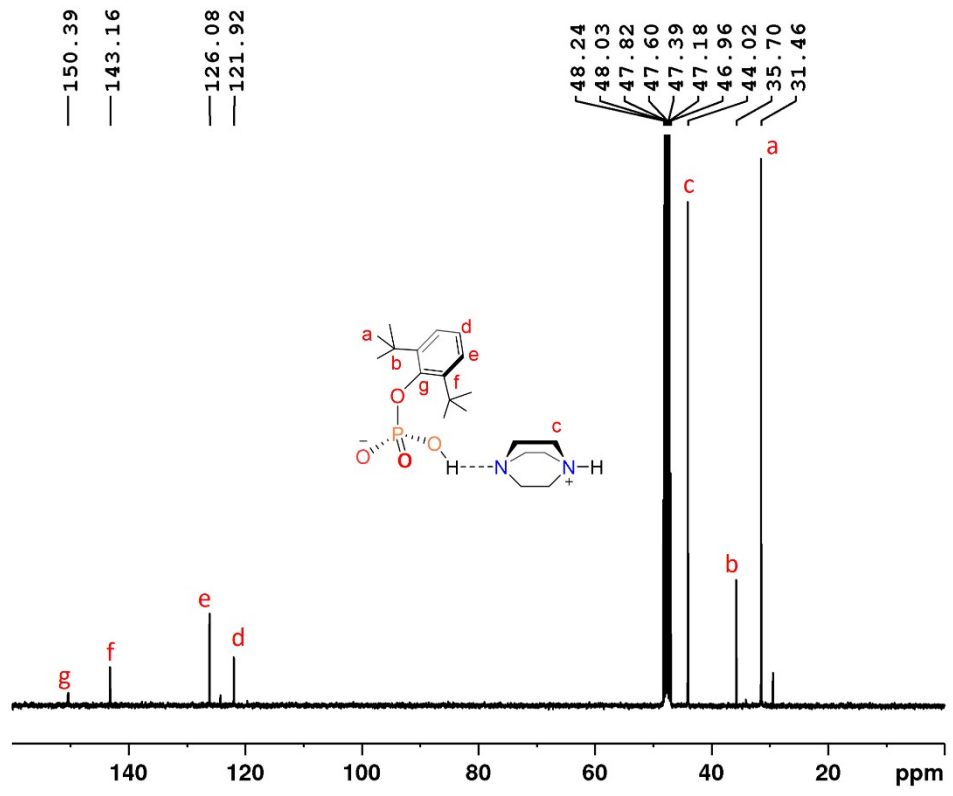


Fig. S16 ^{13}C NMR spectrum (CD_3OD, 100 MHz) of compound **3**.

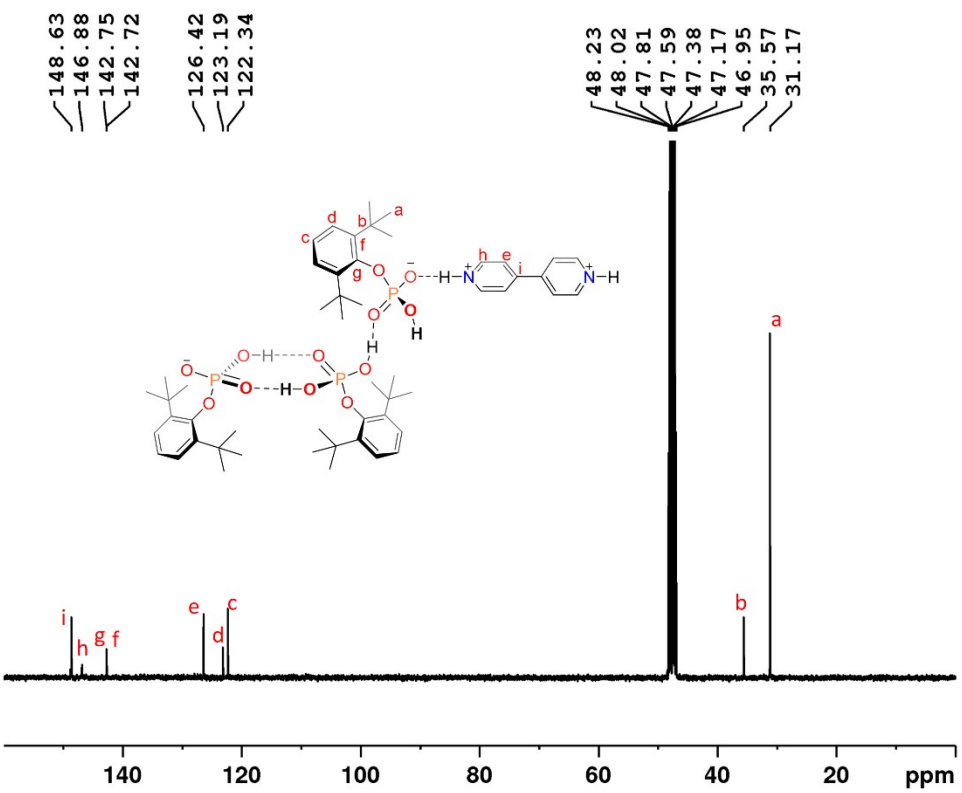


Fig. S17 ^{13}C NMR spectrum (CD_3OD, 100 MHz) of compound **4**.

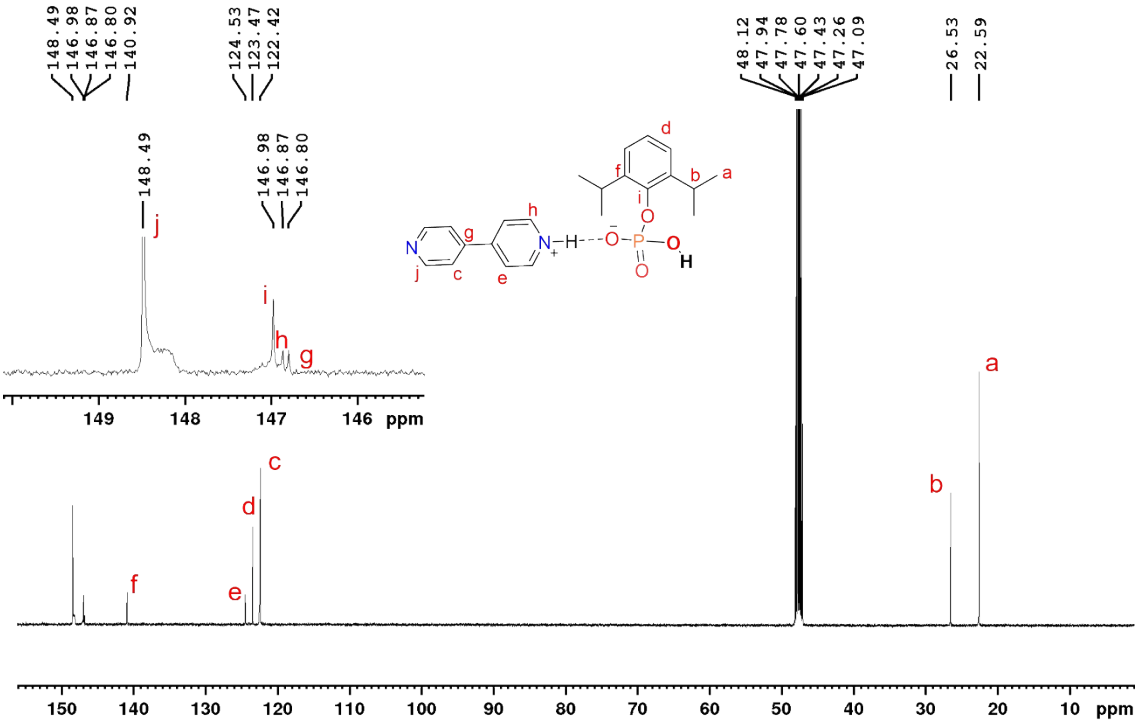


Fig. S18 ^{13}C NMR spectrum (CD_3OD, 125 MHz) of compound **5**.

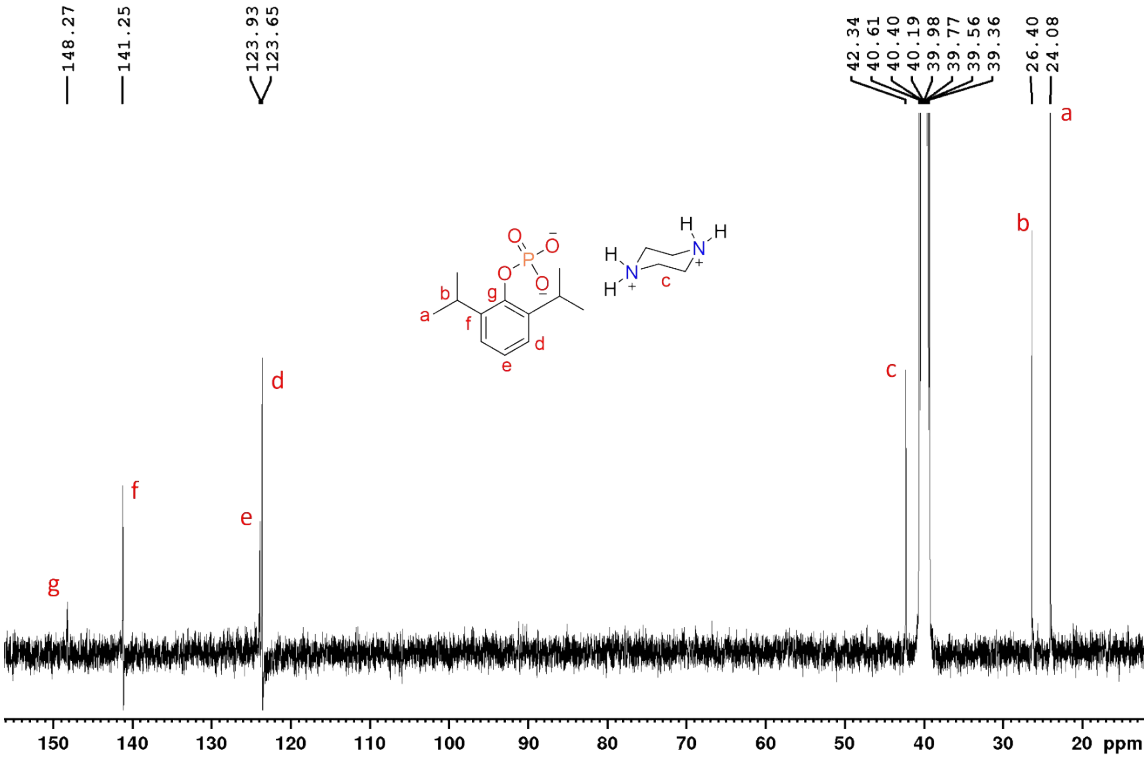


Fig. S19 ^{13}C NMR spectrum (DMSO-d6, 125 MHz) of compound **5**.

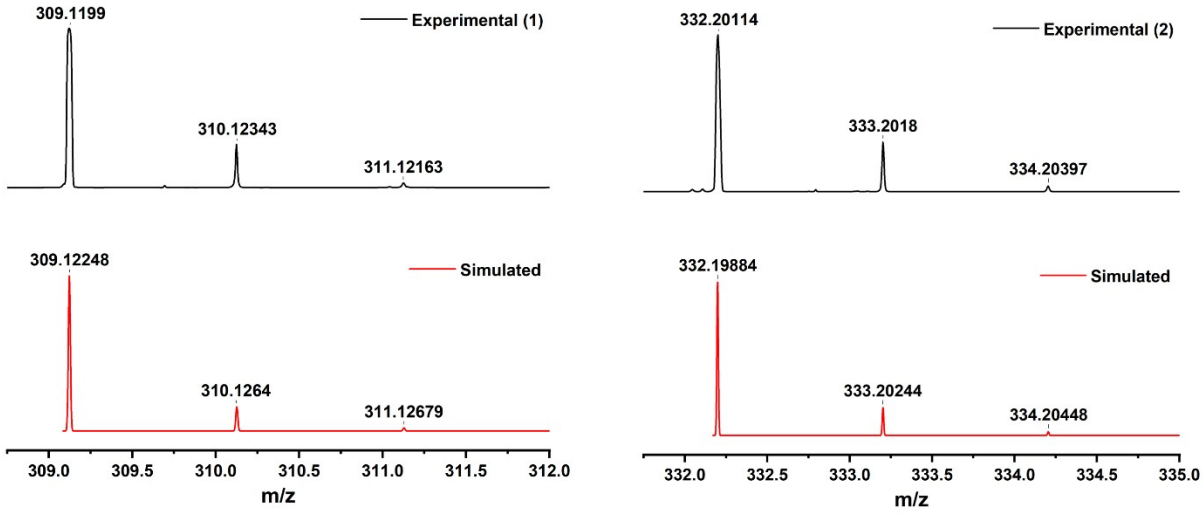


Fig. S20 ESI-MS spectra of the simulated and experimental isotopic patterns $[M+Na]^+$ ion peak for **1**, $[M+H]^+$ ion peak for **2**.

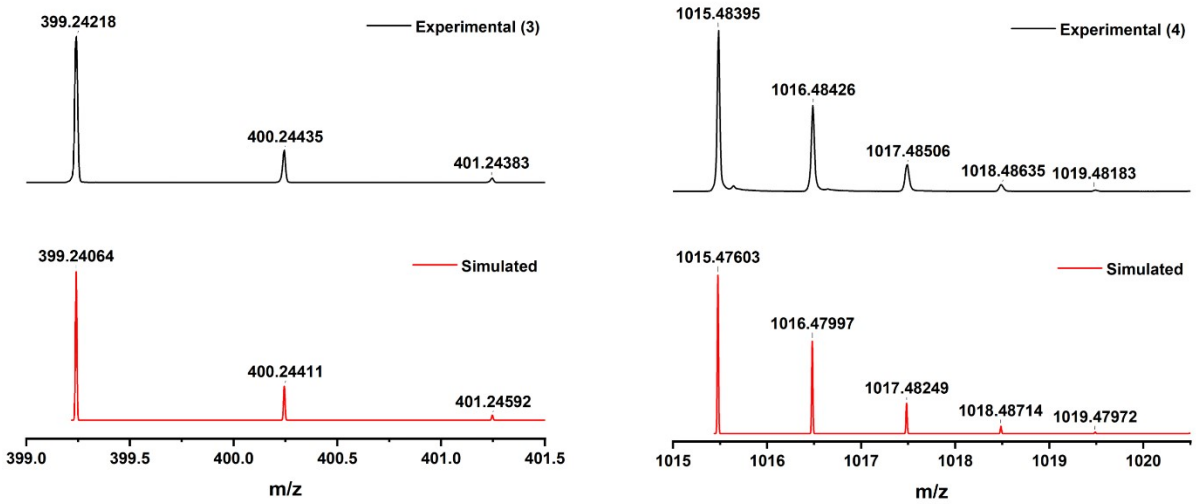


Fig. S21 ESI-MS spectra of the simulated and experimental isotopic patterns $[M+H]^+$ ion peak for **3** and **4**.

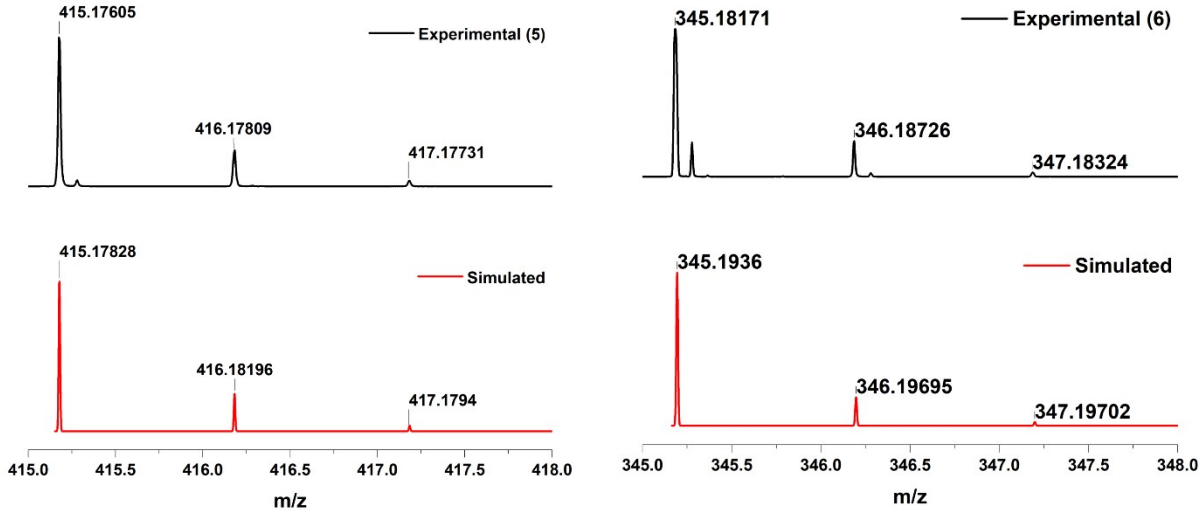


Fig. S22 ESI-MS spectra of the simulated and experimental isotopic patterns $[M+H]^+$ ion peak for **5** and **6**.

Absorption and emission

The UV-vis absorption spectra of compounds **1-6** were recorded in MeOH solution. All the compounds displayed absorption maxima wavelength around 270 nm. In the emission spectra, no apparent emission was observed in compounds **1-5**. Compound **6** shows an emission maximum at 290 nm when excited by 270 nm (**Fig. S23**).

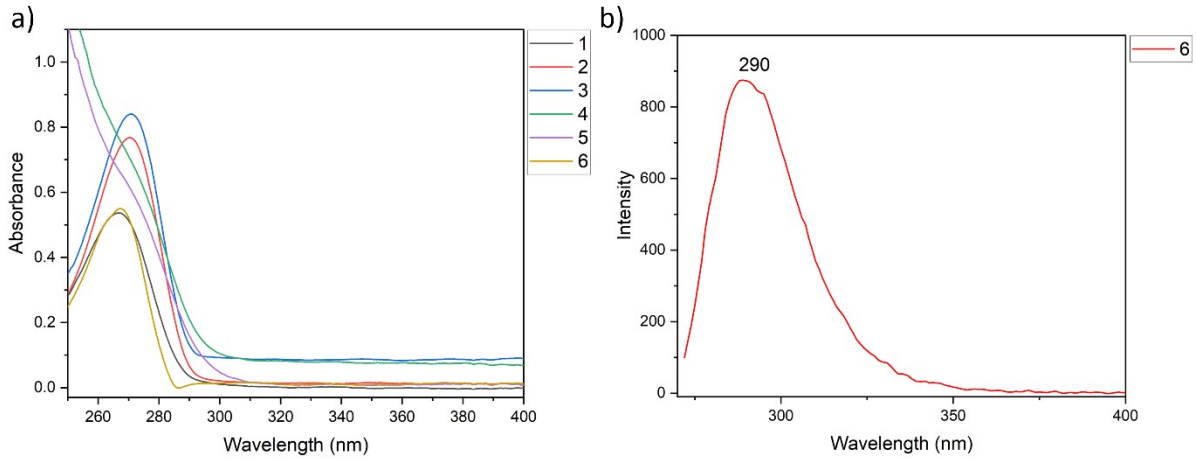


Fig. S23. a) Comparison of absorption spectra of compounds **1-6** ($2x10^{-5}$ M) recorded in MeOH at room temperature. b) Emission spectrum of compound **6** ($2x10^{-5}$M) recorded in MeOH using λ_{ex} = 270 nm.

Hirshfeld surface calculations

The molecular HS and relative 2D fingerprint plots for crystal structures **1-6** were generated using Crystal Explorer 21.5 from their CIF file.[1] HS analysis separates the crystal space into smooth, non-overlapping interlocking molecular volumes to investigate and visualise the intermolecular interactions and packing patterns of the molecules in the crystalline phase. The contacts around the van der Waals radii are depicted in white on the d_{norm} surface, while the shorter and longer intermolecular interactions are red and blue, respectively. Shape index maps have been used to visualise the pair of red hollows and blue bumps in maps that connect the molecule's surface. The curvedness map is a function of the root-mean-square curvature of the surface, with large green patches (corresponding to flat) separated by dark blue borders (high curvedness). The d_i versus d_e graph is a two-dimensional fingerprint plot that identifies the contribution of different types of intermolecular interactions.

Hirshfeld Surface Analyses

The Hirshfeld surfaces (HS) of **1-6** are illustrated in **Fig. S24-S26**, respectively, where the surfaces are mapped with d_{norm}, shape index, and curvedness. Compounds **1-6** exhibit intense red spots, which stand for strong O···H contacts between the phosphate moieties (15.4 -21.6%) or phosphate with dimethylamine cation, bipyridine, DABCO or piperazine N-H (**Fig. S28**). The significantly greater value of the N···H contact (6.4 %) in **5** is mostly due to the interaction of monoprotonated 4,4-bpy with the phosphate's P-OH. Therefore, the crystal packing of all compounds is controlled by the predominance of hydrogen bonding interactions of the types O–H···O and N–H···O. Additionally, the shape index (**Fig. S25**) and curvedness (**Fig. S26**) can be used to represent the typical packing and interactions between adjacent molecules in the crystal. The curvedness is defined as a function of its root mean square curvature of the surface, and there are no flat segments shown by blue contours on the curvedness map, indicating that π-π interactions are not present in crystal structures.

2D fingerprint plots of the Hirshfeld surfaces of all the complexes are depicted in **Fig.S27**. For all the complexes, the H··· H interactions contribute the most to the overall Hirshfeld surface (from 58.5 to 78.7%) (**Fig. S27** and **S28**). Despite the significance of the H···H interaction, the structures are stabilized by close contact of O···H interactions (11.2 to 21.6%) and C···H/H···C (5 to 21.3%). Several spikes of varying lengths and thickness in the fingerprint plots represent the most prominent respective interactions. Among those spikes, the

two at the left corner correspond to the strong O···H/N···H interactions. Additionally, the spike at the left middle is contributed by the H···H interactions. The peripheral spikes at the top right corner correspond to the C···H interaction. The central region of the plot corresponds to the non-directional H···H contacts. The relative contribution of the different interactions to the Hirshfeld surfaces is shown in **Fig. S27**.

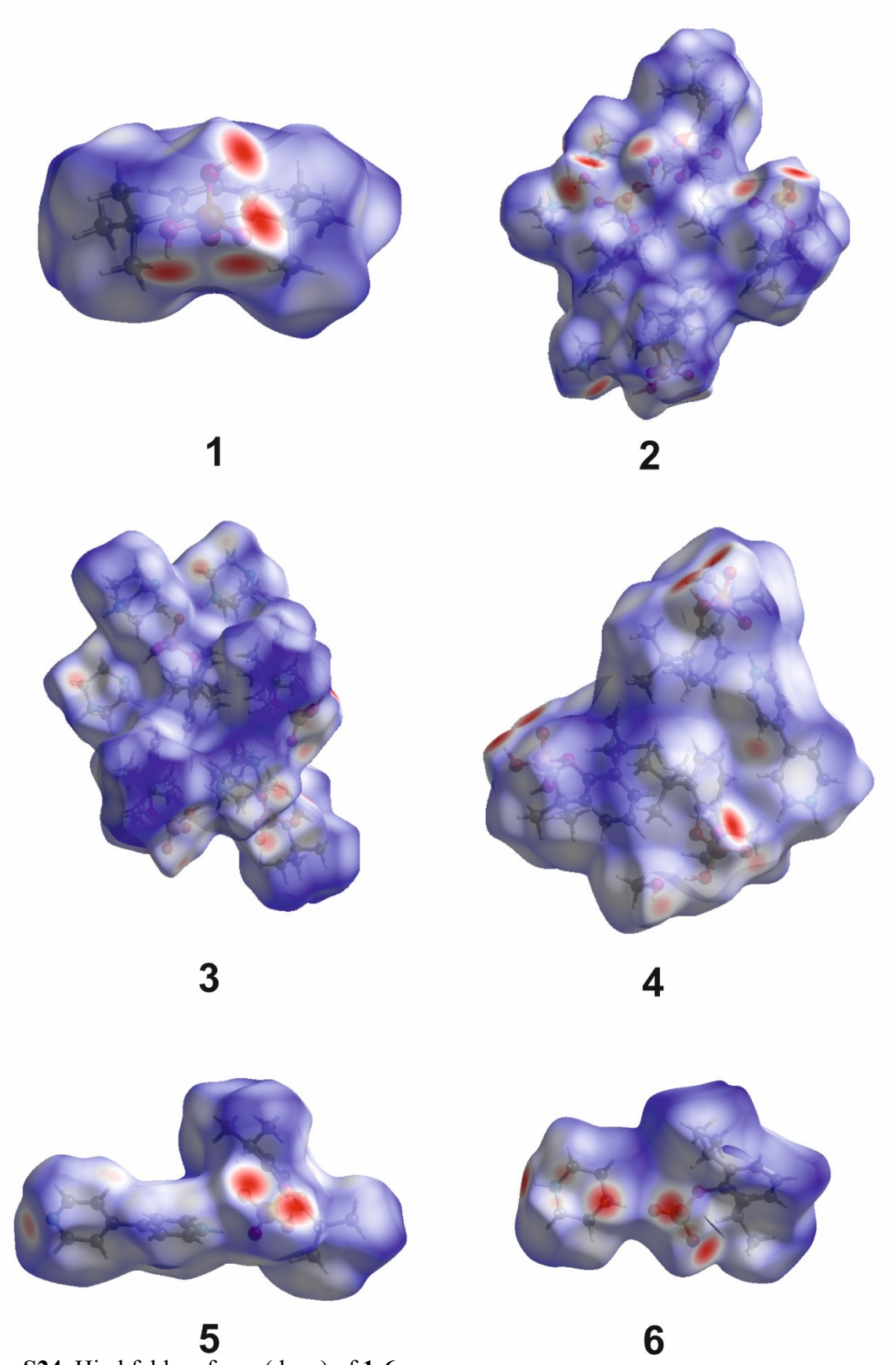


Fig. S24. Hirshfeld surfaces (d_{norm}) of **1**-**6**.

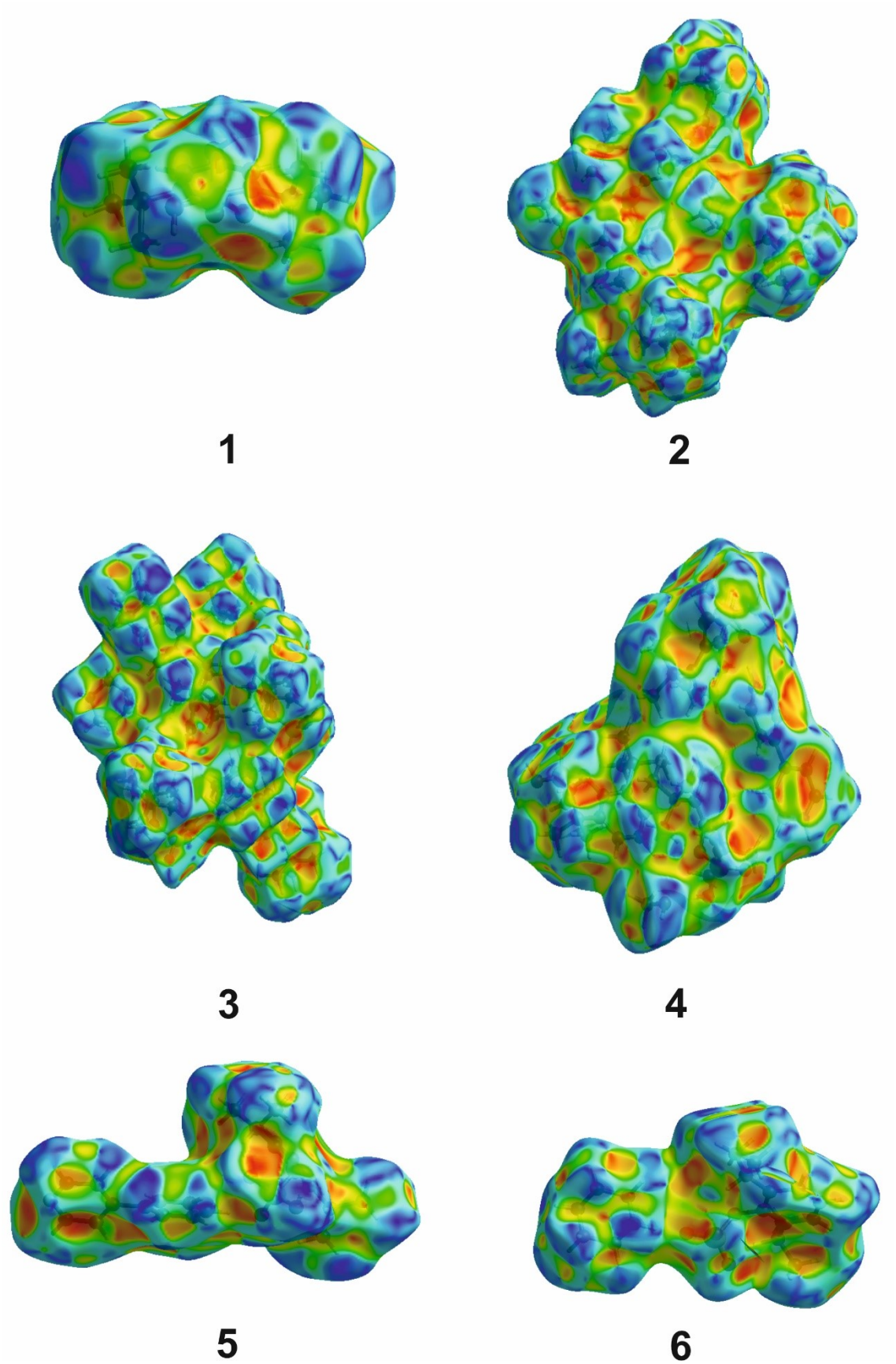


Fig. S25. Hirshfeld surfaces (Shape Index) of **1**-**6**.

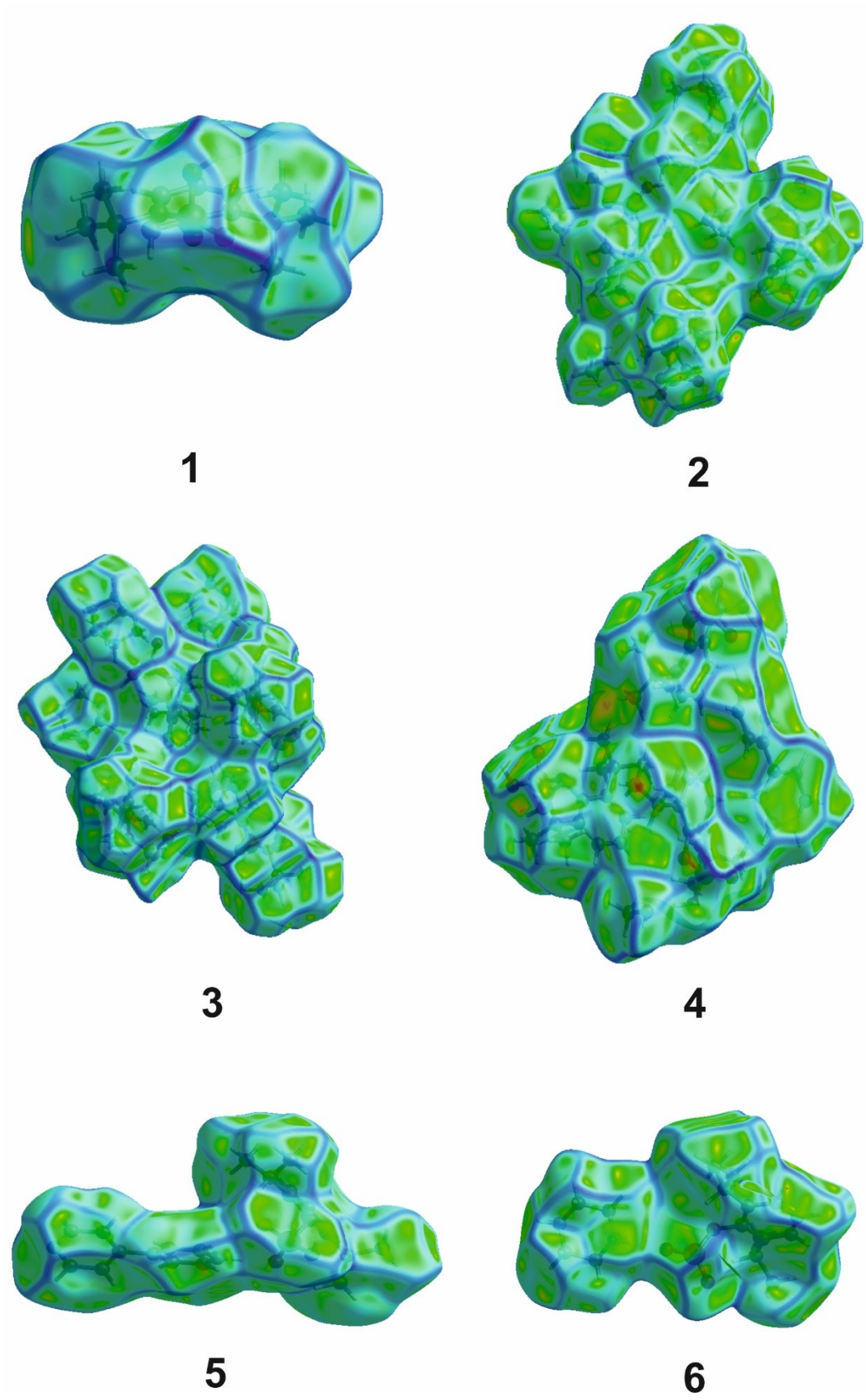


Fig. S26. Hirshfeld surfaces (Curvedness) of **1**-**6**.

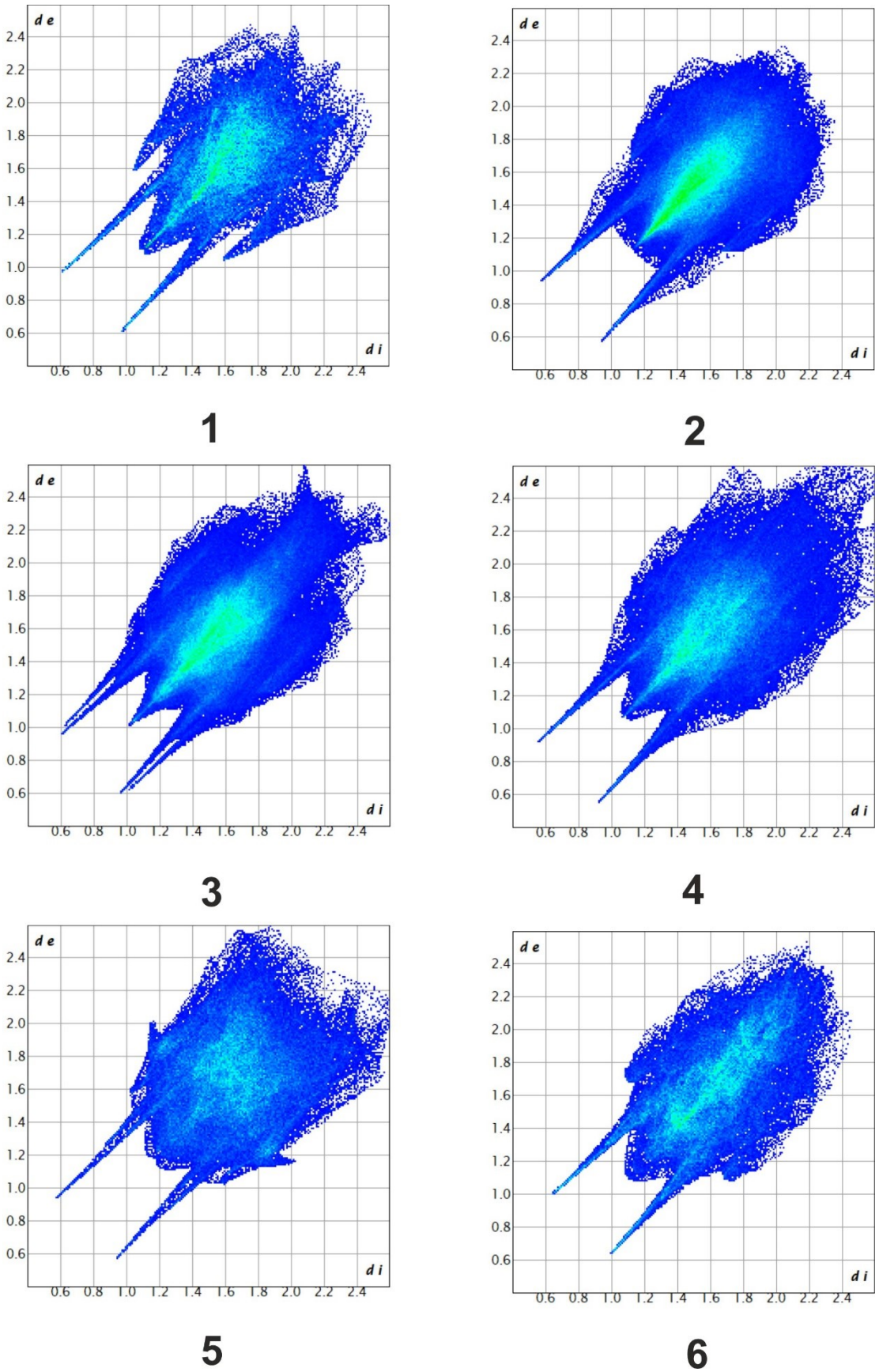
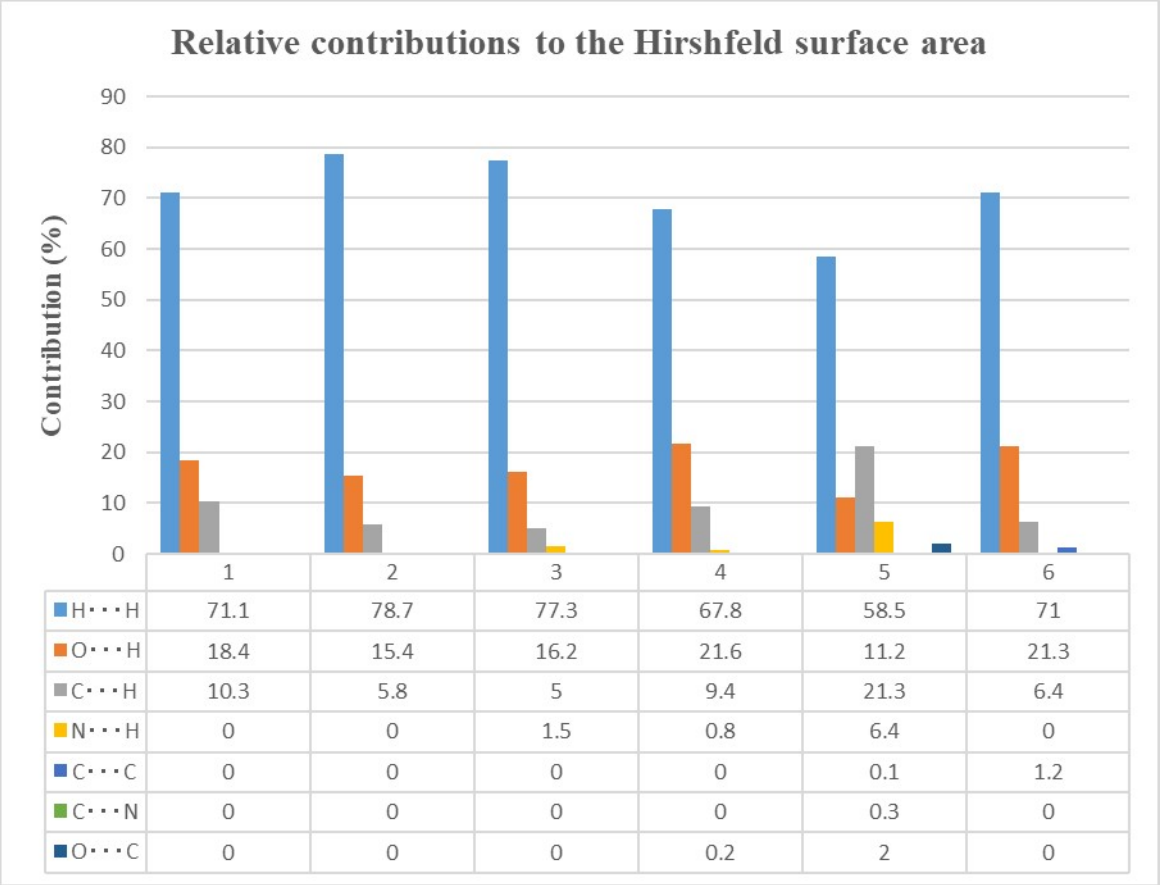


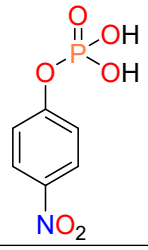
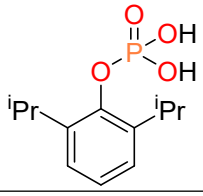
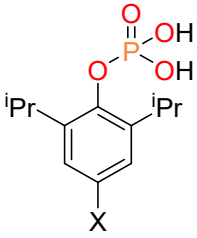
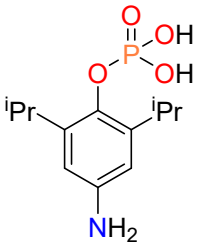
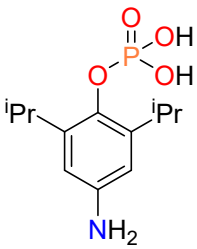
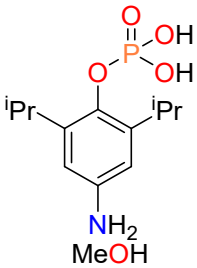
Fig. S27. 2D fingerprint plots (full) with d_i and d_e of **1**-**6**.

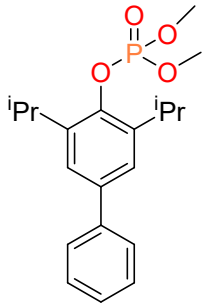
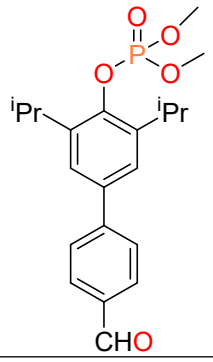
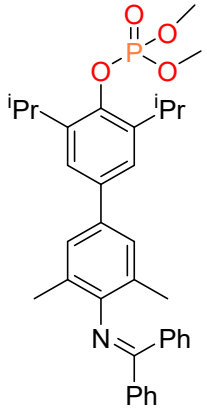
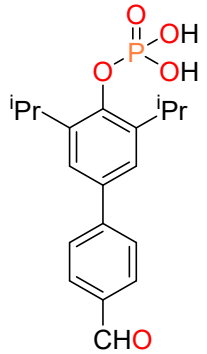
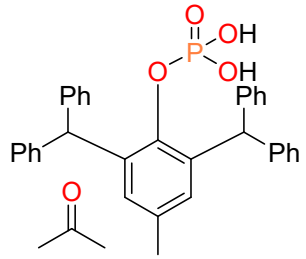


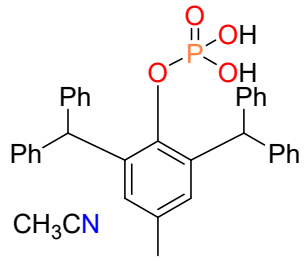
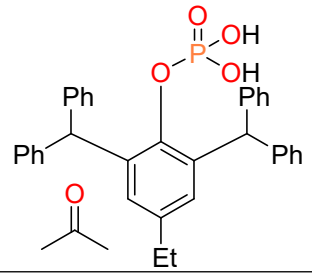
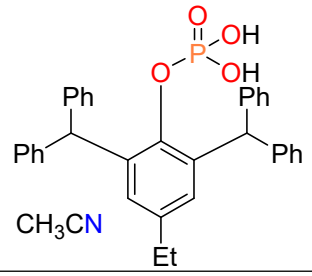
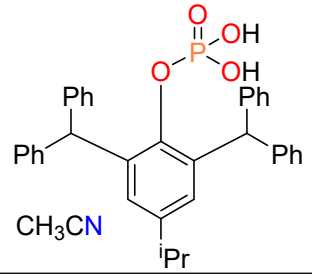
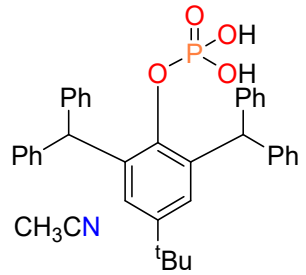
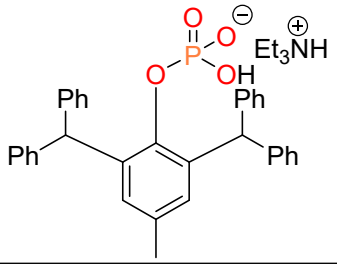
	1	2	3	4	5	6
H···H	71.1	78.7	77.3	67.8	58.5	71
O···H	18.4	15.4	16.2	21.6	11.2	21.3
C···H	10.3	5.8	5	9.4	21.3	6.4
N···H	0	0	1.5	0.8	6.4	0
C···C	0	0	0	0	0.1	1.2
C···N	0	0	0	0	0.3	0
O···C	0	0	0	0.2	2	0

Fig. S28. Contributions (%) of different interactions including the reciprocal contacts.

Table S1. Comparison of H-bonding pattern in the crystal structures of aryl phosphates.

S.No	Compound	Space group	H-bonding type	Ref.
1		Monoclinic $P2_1$	1-D Chain / tape P–OH···O=P	[2]
2		Monoclinic $P2_1$	1-D Chain / tape P–OH···O=P	[3]
3	 X = Cl, Br, I	Monoclinic C2/c	1-D Chain / tubular-well P–OH···O=P	[4]
4	 1/3H_2O MeOH	$P\bar{3}_1c$	Drum-like structure (H_2O dimer)	[5]
5	 1/3H_2O	Monoclinic C2/c	Drum-like Structure (H_2O dimer)	[5]
6	 MeOH	Triclinic $P\bar{1}$	Spherical cage	[5]

7		Monoclinic C2/c	No secondary interaction	[4]
8		Triclinic $P\bar{1}$	Formyl tail to tail interaction	[4]
9		Monoclinic P2/c	No secondary interaction	[4]
10		Monoclinic C2/c	1-D tubular channel	[4]
11		Triclinic $P\bar{1}$	Dimeric	[6, 7]

12		Monoclinic $P2_1/n$	1-D polymeric chain	[6]
13		Triclinic $P\bar{1}$	Dimeric	[6]
14		Triclinic $P\bar{1}$	Dimeric	[6]
15		Triclinic $P\bar{1}$	Dimeric	[6]
16		Triclinic $P\bar{1}$	Dimeric	[6]
17		Triclinic $P\bar{1}$	Dimeric	[6]

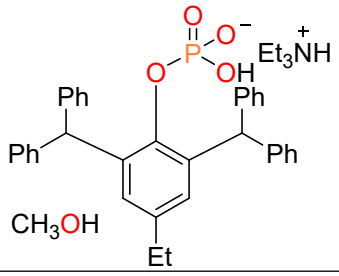
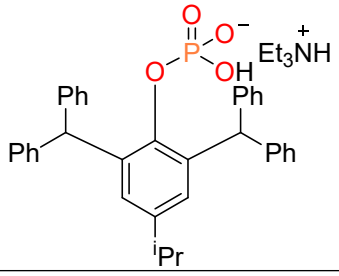
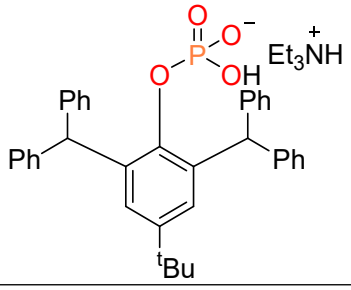
18		Monoclinic $P2_1/n$	Dimeric	[6]
19		Triclinic $P\bar{1}$	Dimeric	[6]
20		Monoclinic $P2_1/n$	Dimeric	[6]

Table S2. Selected bond lengths (Å) of **1**-**6**.

S.No	Compound	P centre	P-O-Ar	P=O	$P-O^-$	P-OH
1	**1**	P1	1.562(3)	1.493(3)		1.536(3)
						1.533(3)
2	**2**	P1	1.6078(13)	1.4724(15)	1.5067(13)	1.5476(16)
		P2	1.6042(13)	1.4855(13)	1.5052(13)	1.5547(13)
		P3	1.6159(12)	1.4868(14)	1.4964(13)	1.5615(13)
		P4	1.6147(13)	1.4832(14)	1.4896(14)	1.5685(13)
3	**3**	P1	1.6332(13)	1.4797(15)	1.5041(13)	1.5616(13)
		P2	1.6381(13)	1.4794(14)	1.4978(13)	1.5672(13)
		P3	1.6330(13)	1.4818(15)	1.4940(13)	1.5674(13)
		P4	1.6346(13)	1.4748(16)	1.4915(14)	1.5628(14)
4	**4**	P1	1.5929(14)	1.4959(15)		1.5295(14)
						1.5326(15)
		P2	1.6067(14)	1.4983(14)	1.5007(14)	1.5564(14)
		P3	1.6105(14)	1.4925(14)	1.5075(14)	1.5493(15)
5	**5**	P1	1.6204(9)	1.498(1)	1.5303(9)	1.5281(10)
6	**6**	P1	1.6375(18)	1.4999(16)	1.4956(16)	
					1.5218(18)	

Table S3. Selected bond lengths (Å) and angles (°) of **1**-**6**.				
1	P(1)—O(1)	1.562(3)	O(2)—P(1)—O(1)	109.75(15)
	P(1)—O(2)	1.493(3)	O(2)—P(1)—O(4)	110.91(15)
	P(1)—O(3)	1.536(3)	O(3)—P(1)—O(1)	107.38(16)
	P(1)—O(4)	1.533(3)	O(4)—P(1)—O(3)	105.79(16)
	O(2)—P(1)—O(3)	114.82(15)	O(4)—P(1)—O(1)	107.90(16)
2	P(1)—O(11)	1.6078(13)	O(13)—P(1)—O(11)	107.81(7)
	P(1)—O(12)	1.4724(15)	O(13)—P(1)—O(14)	109.23(8)
	P(1)—O(13)	1.5067(13)	O(12)—P(1)—O(11)	109.62(8)
	P(1)—O(14)	1.5476(16)	O(12)—P(1)—O(13)	114.52(9)
	P(2)—O(21)	1.6042(13)	O(12)—P(1)—O(14)	113.35(11)
	P(2)—O(22)	1.4855(13)	O(14)—P(1)—O(11)	101.37(9)
	P(2)—O(23)	1.5052(13)	O(23)—P(2)—O(21)	108.31(7)
	P(2)—O(24)	1.5547(13)	O(23)—P(2)—O(24)	109.37(7)
	P(3)—O(31)	1.6159(12)	O(22)—P(2)—O(21)	110.79(7)
	P(3)—O(32)	1.4868(14)	O(22)—P(2)—O(23)	114.58(8)
	P(3)—O(33)	1.4964(13)	O(22)—P(2)—O(24)	112.95(8)
	P(3)—O(34)	1.5615(13)	O(24)—P(2)—O(21)	99.76(7)
	P(4)—O(41)	1.6147(13)	O(32)—P(3)—O(31)	107.84(7)
	P(4)—O(42)	1.4832(14)	O(32)—P(3)—O(34)	111.33(7)
	P(4)—O(43)	1.4896(14)	O(32)—P(3)—O(33)	117.21(8)
	P(4)—O(44)	1.5685(13)	O(34)—P(3)—O(31)	104.53(7)
	O(33)—P(3)—O(31)	109.70(7)	O(42)—P(4)—O(44)	110.95(7)
	O(33)—P(3)—O(34)	105.50(7)	O(42)—P(4)—O(43)	119.65(8)
	O(44)—P(4)—O(41)	104.39(7)	O(43)—P(4)—O(41)	109.17(7)
	O(42)—P(4)—O(41)	106.16(7)	O(43)—P(4)—O(44)	105.55(8)
3	P(1)—O(11)	1.6332(13)	O(12)—P(1)—O(14)	111.20(8)
	P(1)—O(12)	1.4797(15)	O(12)—P(1)—O(13)	118.12(9)
	P(1)—O(13)	1.5041(13)	O(24)—P(2)—O(21)	104.47(7)
	P(1)—O(14)	1.5616(13)	O(23)—P(2)—O(21)	102.60(7)
	P(2)—O(21)	1.6381(13)	O(23)—P(2)—O(24)	108.17(8)
	P(2)—O(22)	1.4794(14)	O(22)—P(2)—O(21)	111.03(8)
	P(2)—O(23)	1.4978(13)	O(22)—P(2)—O(24)	110.93(8)
	P(2)—O(24)	1.5672(13)	O(22)—P(2)—O(23)	118.50(8)
	P(3)—O(31)	1.6330(13)	O(33)—P(3)—O(31)	102.74(7)
	P(3)—O(32)	1.4818(15)	O(33)—P(3)—O(34)	108.83(8)
	P(3)—O(33)	1.4940(13)	O(32)—P(3)—O(31)	110.84(8)

	P(3)—O(34)	1.5674(13)	O(32)—P(3)—O(33)	118.54(9)
	P(4)—O(41)	1.6346(13)	O(32)—P(3)—O(34)	110.12(8)
	P(4)—O(42)	1.4748(16)	O(34)—P(3)—O(31)	104.70(7)
	P(4)—O(43)	1.4915(14)	O(44)—P(4)—O(41)	104.42(7)
	P(4)—O(44)	1.5628(14)	O(42)—P(4)—O(41)	110.50(8)
	O(14)—P(1)—O(11)	105.33(7)	O(42)—P(4)—O(44)	110.50(9)
	O(13)—P(1)—O(11)	102.06(7)	O(42)—P(4)—O(43)	119.28(10)
	O(13)—P(1)—O(14)	108.21(8)	O(43)—P(4)—O(41)	102.84(7)
	O(12)—P(1)—O(11)	110.86(8)	O(43)—P(4)—O(44)	108.09(9)
4	P(1)—O(1)	1.5929(14)	O(2)—P(1)—O(4)	114.96(8)
	P(1)—O(2)	1.4959(15)	O(4)—P(1)—O(1)	105.37(8)
	P(1)—O(3)	1.5295(14)	O(24)—P(2)—O(21)	100.21(7)
	P(1)—O(4)	1.5326(15)	O(22)—P(2)—O(21)	112.27(8)
	P(2)—O(21)	1.6067(14)	O(2)—P(1)—O(3)	112.03(8)
	P(2)—O(22)	1.4983(14)	O(22)—P(2)—O(24)	106.37(8)
	P(2)—O(23)	1.5007(14)	O(22)—P(2)—O(23)	115.15(8)
	P(2)—O(24)	1.5564(14)	O(23)—P(2)—O(21)	108.86(7)
	P(3)—O(31)	1.6105(14)	O(23)—P(2)—O(24)	113.03(8)
	P(3)—O(32)	1.4925(14)	O(33)—P(3)—O(31)	105.83(8)
	P(3)—O(33)	1.5075(14)	O(33)—P(3)—O(34)	110.07(8)
	P(3)—O(34)	1.5493(15)	O(32)—P(3)—O(31)	110.06(8)
	O(3)—P(1)—O(1)	107.39(8)	O(32)—P(3)—O(33)	114.84(8)
	O(3)—P(1)—O(4)	109.40(8)	O(32)—P(3)—O(34)	110.47(9)
	O(2)—P(1)—O(1)	107.19(8)	O(34)—P(3)—O(31)	105.02(8)
	P(1)—O(1)	1.6204(9)	O(2)—P(1)—O(3)	112.42(5)
	P(1)—O(2)	1.498(1)	O(2)—P(1)—O(4)	113.35(6)
5	P(1)—O(3)	1.5303(9)	O(3)—P(1)—O(1)	107.01(5)
	P(1)—O(4)	1.5281(10)	O(4)—P(1)—O(1)	103.68(5)
	O(2)—P(1)—O(1)	108.29(5)	O(4)—P(1)—O(3)	111.47(5)
	P(1)—O(4)	1.5218(18),	O(2)—P(1)—O(4)	111.29(10)
	P(1)—O(1)	1.6375(18)	O(2)—P(1)—O(1)	107.96(9)
6	P(1)—O(2)	1.4999(16)	O(3)—P(1)—O(4)	112.11(10)
	P(1)—O(3)	1.4956(16)	O(3)—P(1)—O(1)	101.77(9)
	O(4)—P(1)—O(1)	105.96(9)	O(3)—P(1)—O(2)	116.66(10)

Table S4 Hydrogen bond parameters for **1**.

D-H···A	d(D-H) [Å]	d(H···A) [Å]	d(D···A) [Å]	∠DHA [°]
O3-H3···O2^{i}	0.830(19)	1.75(2)	2.573(4)	172.(4)
O4-H4···O2^{ii}	0.840(19)	1.78(2)	2.622(4)	178.(4)

(i) 2-x, 1-y, 1-z; (ii) 1-x, 1-y, 1-z.

Table S5 Hydrogen bond parameters for **2**.

D-H···A	d(D-H) [Å]	d(H···A) [Å]	d(D···A) [Å]	∠DHA [°]
O34-H34···O13	0.850(14)	1.687(14)	2.5297(15)	171.0(19)
O44-H44···O23^{i}	0.827(14)	1.720(14)	2.5471(15)	177.(2)
O2W-H2WB···O32	1.0100	1.8400	2.8276(16)	165.700
O2W-H2WB···O33	1.0100	2.6500	3.1438(16)	110.500
O24-H24···O2W^{ii}	0.881(14)	1.638(14)	2.5182(16)	175.9(19)
O14-H14···O1W	0.860(15)	1.617(16)	2.475(2)	174.(2)
N2-H2A···O23^{i}	0.893(14)	1.840(15)	2.7298(18)	174.1(18)
N2-H2B···O12^{i}	0.897(14)	1.728(14)	2.6240(19)	176.9(19)
N3-H3A···O43^{iii}	0.900(14)	1.807(15)	2.6782(18)	162.1(18)
N3-H3B···O34	0.900(14)	2.525(17)	3.1446(18)	126.4(15)
N3-H3B···O33	0.900(14)	1.952(15)	2.8402(18)	168.7(17)
N4-H4B···O44^{iii}	0.901(14)	2.485(18)	3.1358(19)	129.5(15)
N4-H4B···O43^{iii}	0.901(14)	1.977(15)	2.8565(18)	165.1(18)
N1-H1A···O22	0.874(14)	1.849(15)	2.7060(18)	166.4(19)
N1-H1B···O13	0.897(14)	1.844(15)	2.7373(19)	173.0(19)
O1W-H1WA···O22^{ii}	0.8700	2.0200	2.837(2)	155.400
O1W-H1WB···O32	0.8700	2.0500	2.6927(19)	130.200

(i) -0.5+x, 0.5-y, 0.5+z; (ii) 1-x, 1-y, 1-z; (iii) -0.5+x, 0.5-y, -0.5+z.

Table S6 Hydrogen bond parameters for **3**.

D-H···A	d(D-H) [Å]	d(H···A) [Å]	d(D···A) [Å]	∠DHA [°]
O24-H24···N3^{i}	0.868(14)	1.766(15)	2.6213(19)	168.(2)
O14-H14···N5	0.877(14)	1.751(15)	2.615(2)	168.(2)
O34-H34···N7	0.901(14)	1.747(15)	2.638(2)	169.(2)
O44-H44···N1^{i}	0.871(15)	1.789(15)	2.647(2)	168.(2)
N6-H6···O43^{ii}	0.895(14)	1.696(15)	2.583(2)	170.9(19)
N4-H4A···O33^{ii}	0.894(14)	1.700(15)	2.5876(19)	171.6(19)
N2-H2···O13	0.898(14)	1.664(15)	2.5598(19)	175.(2)
N8-H8···O23	0.881(14)	1.703(15)	2.5833(19)	178.(2)
C14N-H14D···O32^{ii}	0.9900	2.3100	3.115(2)	137.700
C14N-H14E···O23^{iii}	0.9900	2.3700	3.338(2)	167.000
C20N-H20A···O43^{iv}	0.9900	2.2900	3.225(2)	158.000
C20N-H20B···O42	0.9900	2.2400	3.107(2)	145.300
C10N-H10D···O13^{v}	0.9900	2.4300	3.407(2)	171.200
C10N-H10E···O14	0.9900	2.5100	3.430(2)	155.400
C13N-H13D···O22^{iii}	0.9900	2.6000	3.332(2)	130.800
C9N-H9NA···O13	0.9900	2.3300	3.279(2)	159.600
C9N-H9NB···O12^{v}	0.9900	2.4800	3.264(2)	135.400
C2N-H2NA···O24^{vi}	0.9900	2.3300	3.317(2)	174.800
C2N-H2NB···O33^{vii}	0.9900	2.3700	3.278(3)	153.000
C1N-H1NA···O34^{vii}	0.9900	2.6200	3.498(3)	147.600
C1N-H1NB···O23^{vi}	0.9900	2.5300	3.331(2)	137.800
C22N-H22D···O42	0.9900	2.5100	3.334(3)	141.000
C8N-H8NB···O12^{v}	0.9900	2.4400	3.246(3)	138.200
C16N-H16A···O22^{iii}	0.9900	2.5000	3.267(3)	134.200
C3N-H3NB···O34^{vii}	0.9900	2.6200	3.491(3)	146.500

(i) -0.5-x, -0.5+y, 0.5-z; (ii) 0.5-x, 0.5+y, 0.5-z; (iii) 0.5+x, 0.5-y, 0.5+z; (iv) -x, -y, -z; (v) -x, 1-y, 1-z; (vi) -0.5-x, 0.5+y, 0.5-z; (vii) -0.5+x, 0.5-y, 0.5+z.

Table S7 Hydrogen bond parameters for **4**.

D-H···A	d(D-H) [Å]	d(H···A) [Å]	d(D···A) [Å]	∠DHA [°]
O24-H24···O1M	0.824(16)	1.770(17)	2.589(2)	172.(2)
O3-H3···O33^{i}	0.855(16)	1.623(17)	2.4701(19)	171.(2)
O34-H34···O2^{i}	0.836(16)	1.710(17)	2.546(2)	177.(3)
O4-H4···O23^{ii}	0.858(16)	1.607(17)	2.463(2)	176.(3)
N1-H1···O22^{iii}	0.887(16)	1.763(16)	2.647(2)	174.(2)
N2-H2···O32	0.895(16)	1.638(16)	2.527(2)	171.(2)
O1M-H1M···O22^{iv}	0.95(3)	2.29(3)	3.099(2)	142.(3)
C43-H43···O22	0.9500	2.3400	3.252(2)	160.100
C49-H49···O2^{v}	0.9500	2.2900	3.212(2)	162.700

(i) 2-x, -y, 1-z; (ii) x, -1+y, z; (iii) 2-x, 1-y, 2-z; (iv) 1-x, 1-y, 2-z; (v) x, 1+y, z.

Table S8 Hydrogen bond parameters for **5**.

D-H···A	d(D-H) [Å]	d(H···A) [Å]	d(D···A) [Å]	∠DHA [°]
C22-H22···O4^{i}	0.9500	2.4700	3.3418(17)	152.000
O4-H4···O3^{ii}	0.891(15)	1.631(15)	2.5210(13)	178.(2)
N1-H1···O2	0.940(15)	1.616(15)	2.5550(14)	175.8(19)

(i) 1-x, 1-y, 1-z; (ii) -x, 1-y, 1-z.

Table S9 Hydrogen bond parameters for **6**.

D-H···A	d(D-H) [Å]	d(H···A) [Å]	(D···A) [Å]	∠DHA [°]
N2-H2A···O4^{i}	1.02(4)	1.64(4)	2.647(3)	169.(4)
N2-H2B···O2^{ii}	0.891(19)	1.754(19)	2.645(3)	178.(4)
N1-H1A···O4^{iii}	0.933(18)	1.752(19)	2.683(3)	176.(4)
N1-H1B···O3	0.920(19)	1.68(2)	2.590(3)	171.(4)

(i) 1.5-x, 0.5+y, z; (ii) 2-x, 0.5+y, 1.5-z; (iii) 0.5+x, y, 1.5-z

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