Supporting Information for

"Synthetic Strategies to Further-Functionalised Phosphate Primary Building Units (PBUs): Crystal Structures and Solid-state Aggregation Behavior in a Series of Para-halo, Formylphenyl, and Aminophenyl Substituted Monoaryl Phosphates"

Aijaz A. Dar,[a] Abhijit Mallick[a] and Ramaswamy Murugavel[a]*

Figure 20. ^{13}C NMR of **14** (DMSO-*d,* and CD_3OD, 125 MHz)

Figure S21. ESI-HRMS (negative mode) of compound **8** (Mw = 362.06)

Table S1. Comparison of H-bonding pattern of compounds with -X-PO_3H_2 functionalities (X = main group element P or Si)

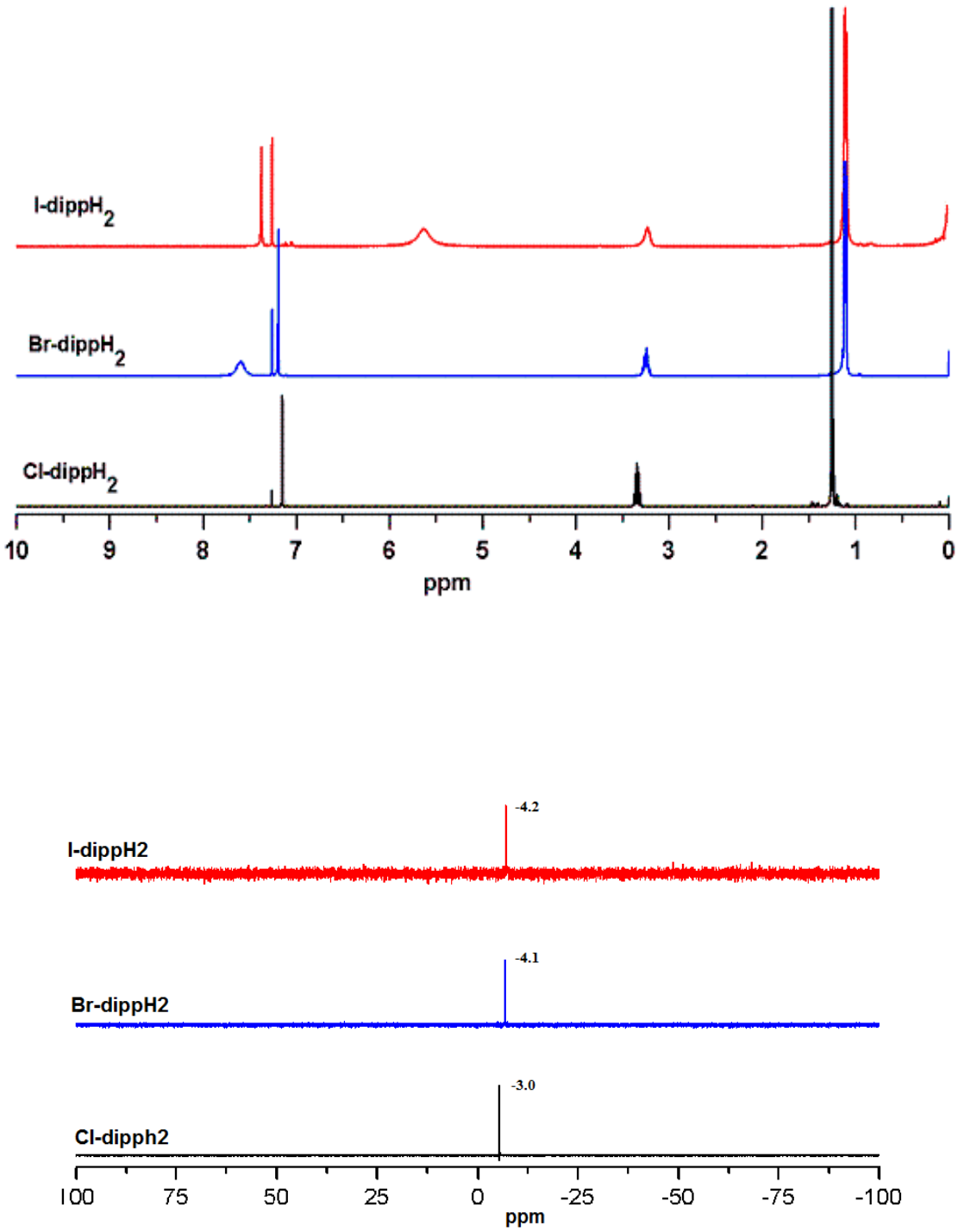


Figure S1. ^{1}H NMR (400 MHz, top) and ^{31}P NMR (161 MHz, bottom) spectra of halide functionalized X-dippH$_2$ ligands, **1-3** in DMSO-d_6.

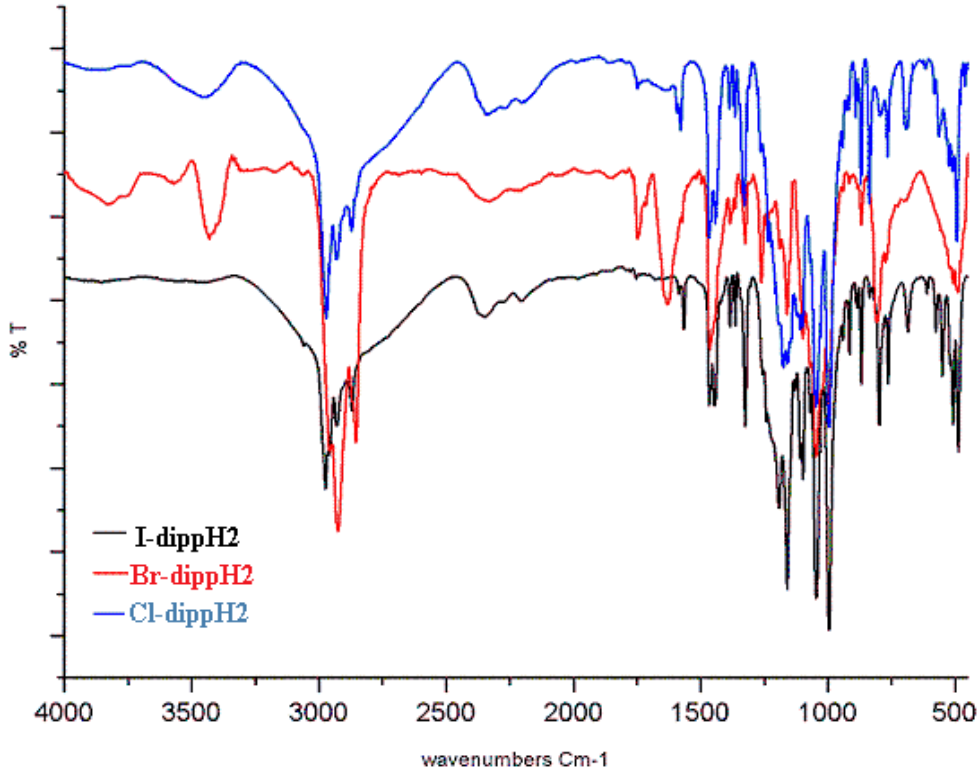


Figure S2. FT-IR spectra of compounds **1-3** (as KBr disc)

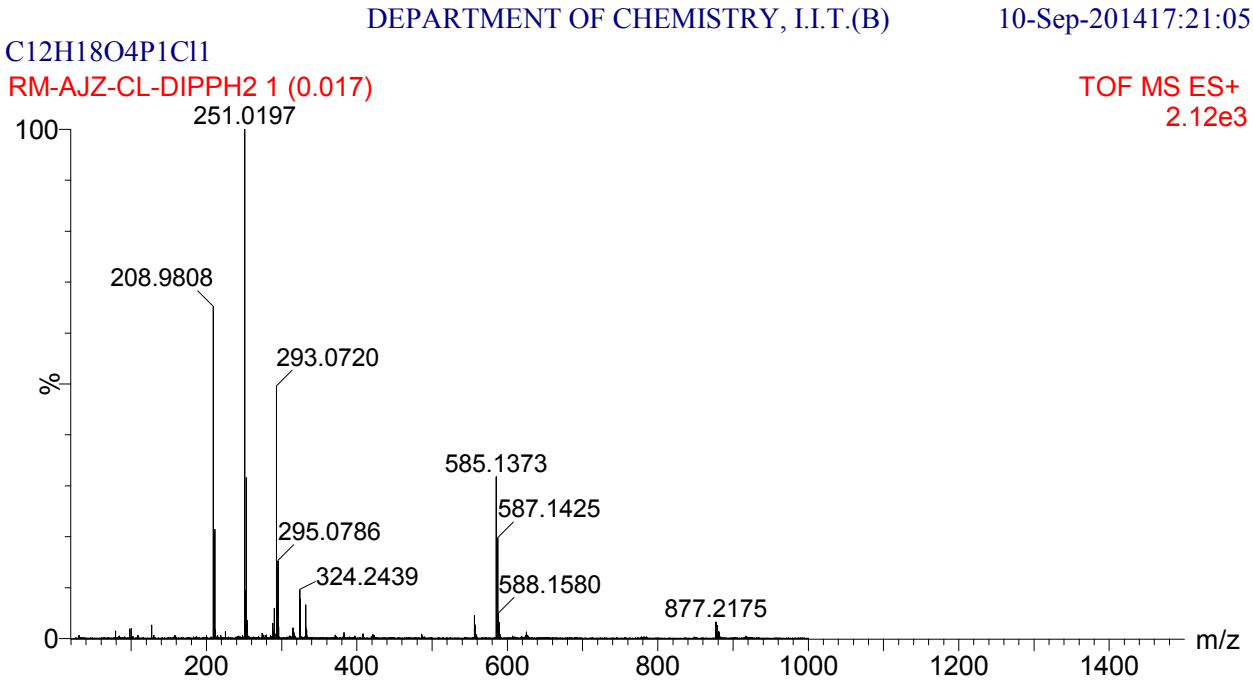


Figure S3. ESI-HRMS of compound **1** (Mw = 292.06)

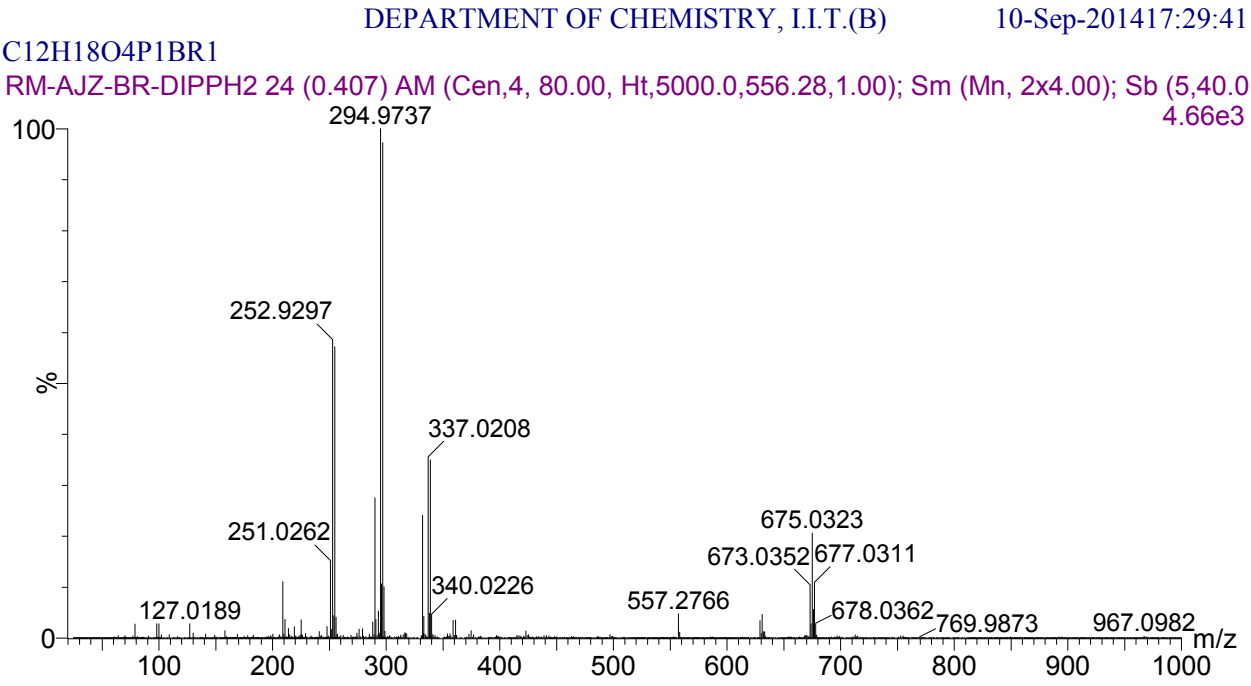


Figure S4. ESI-HRMS of compound **2** (Mw = 336.01)

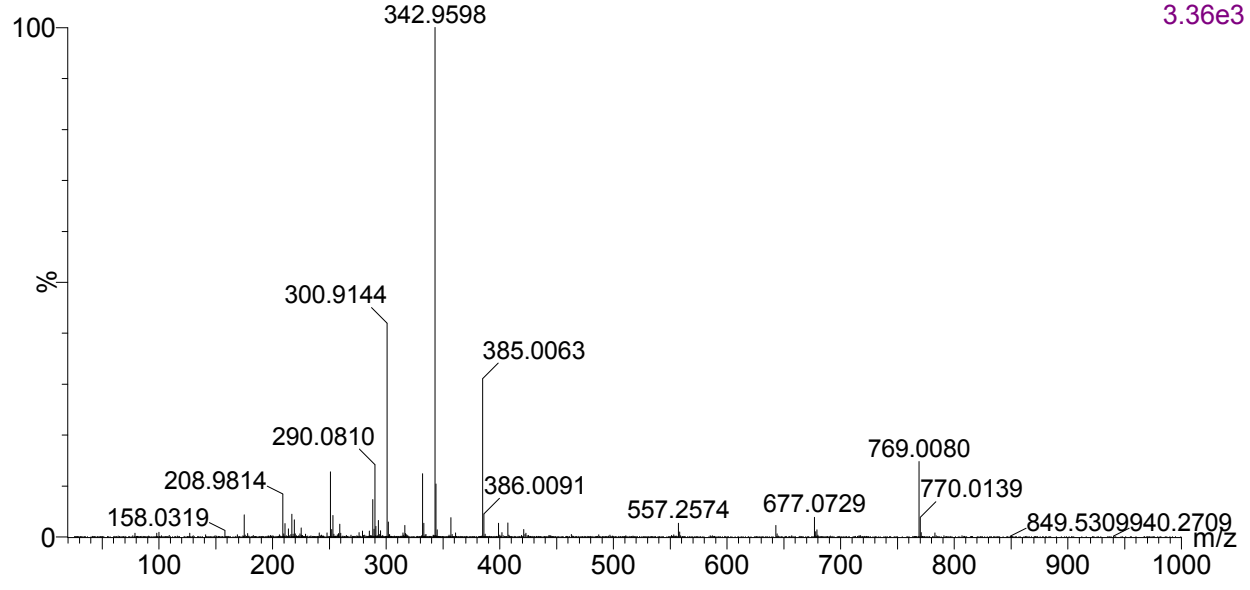


Figure S5. ESI-HRMS of compound **3** (Mw = 383.99)

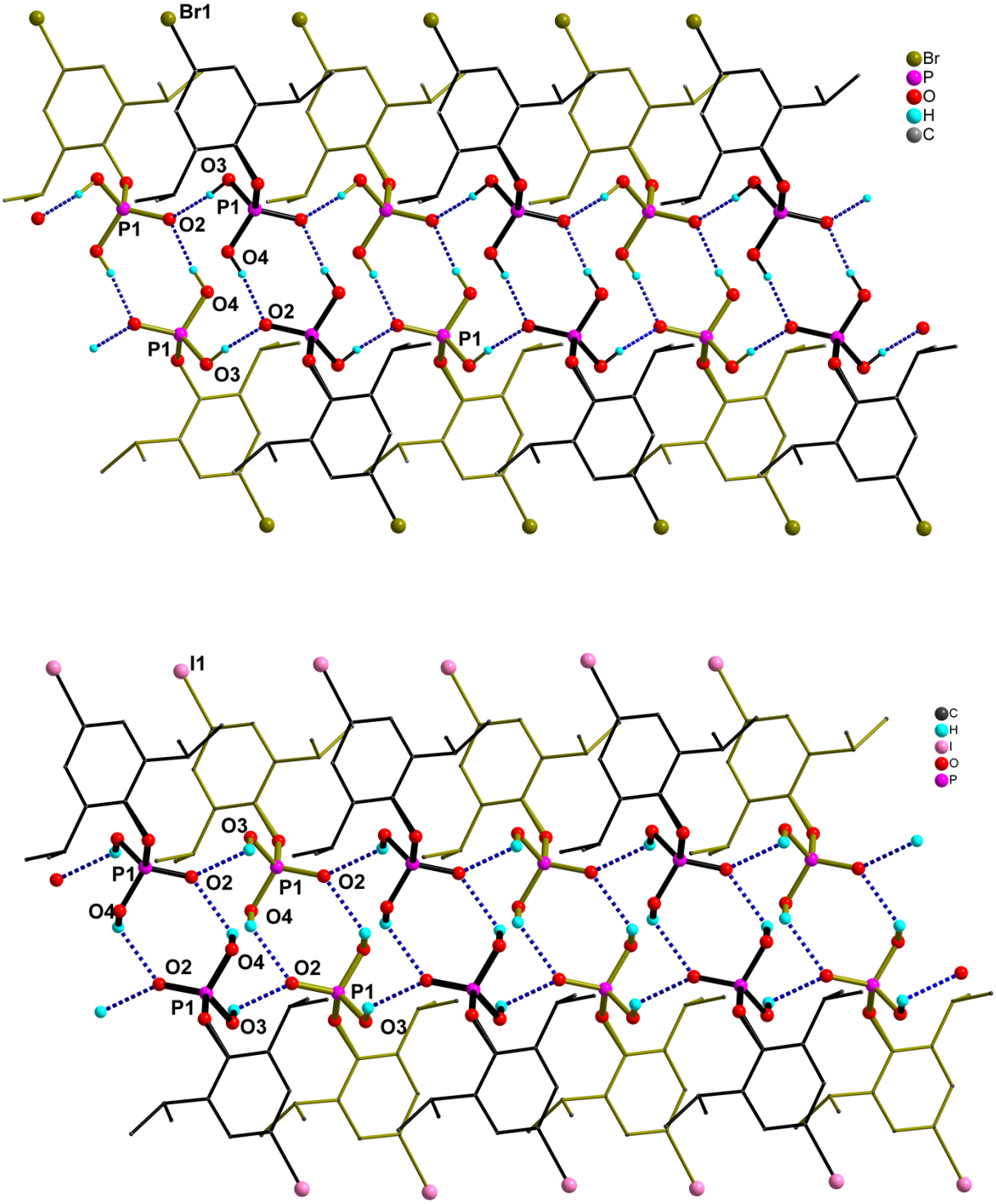


Figure S6. Hydrogen bonding diagrams of **2** and **3**.

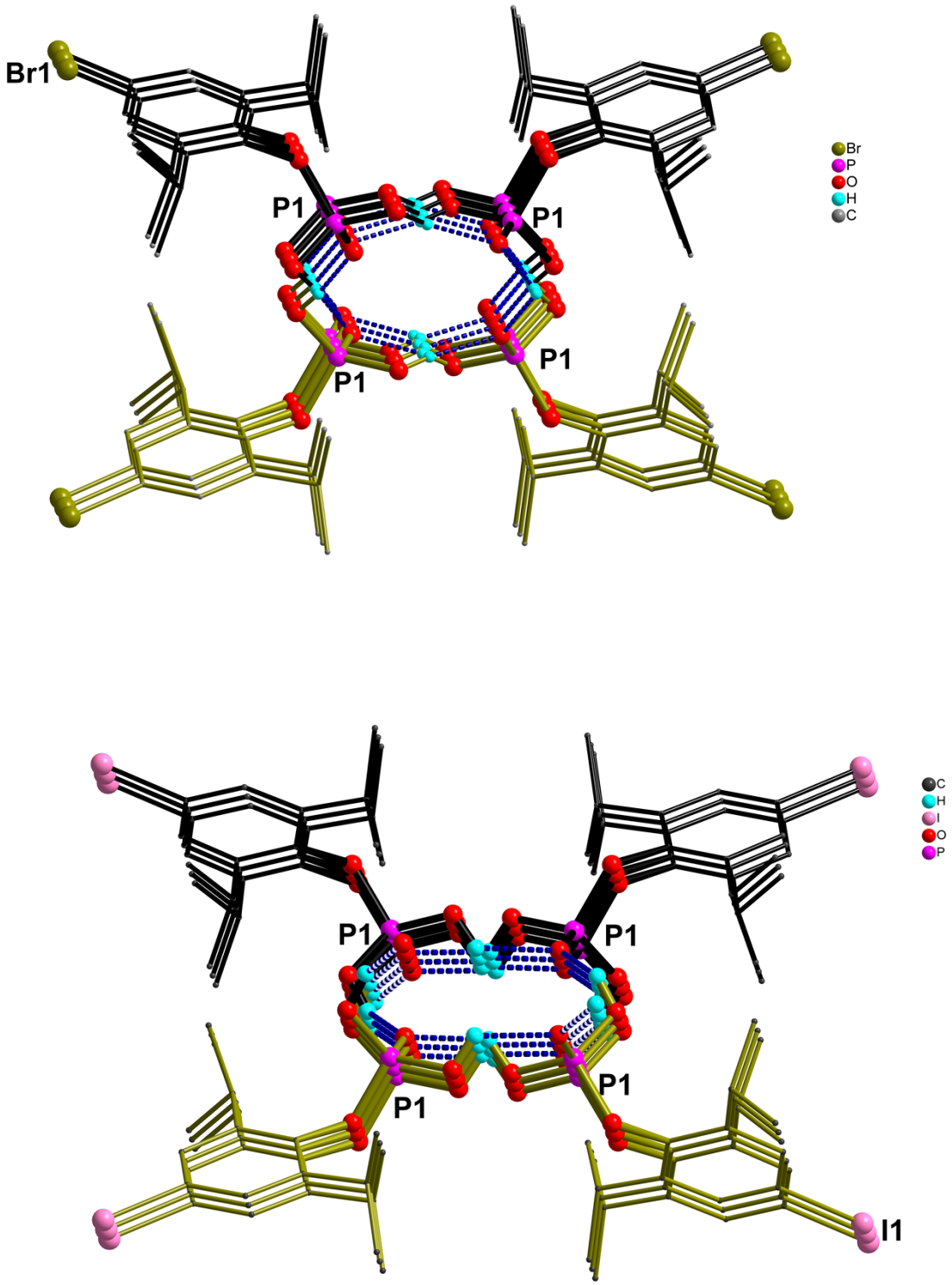


Figure S7. Hydrogen bonding diagrams of **2** and **3**, along *c* axis.

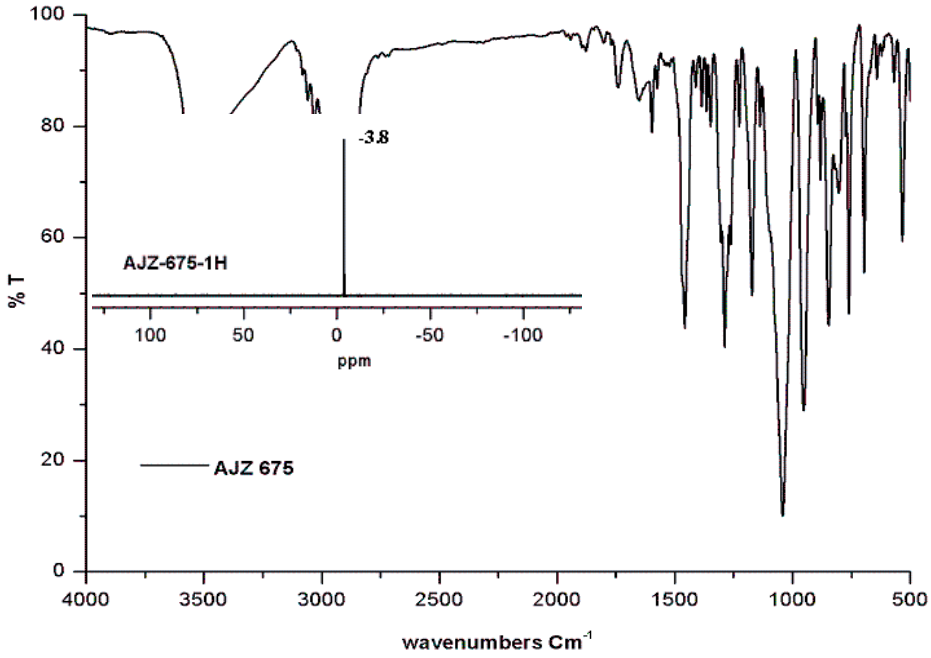


Figure S8. FT-IR spectra of compound **5** (KBr disc)

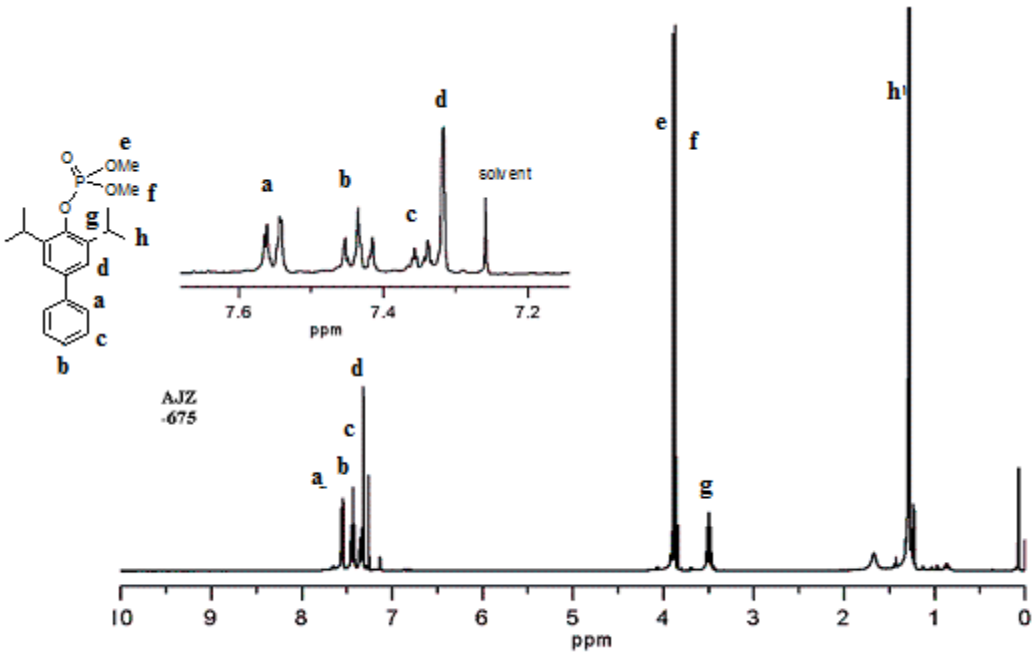
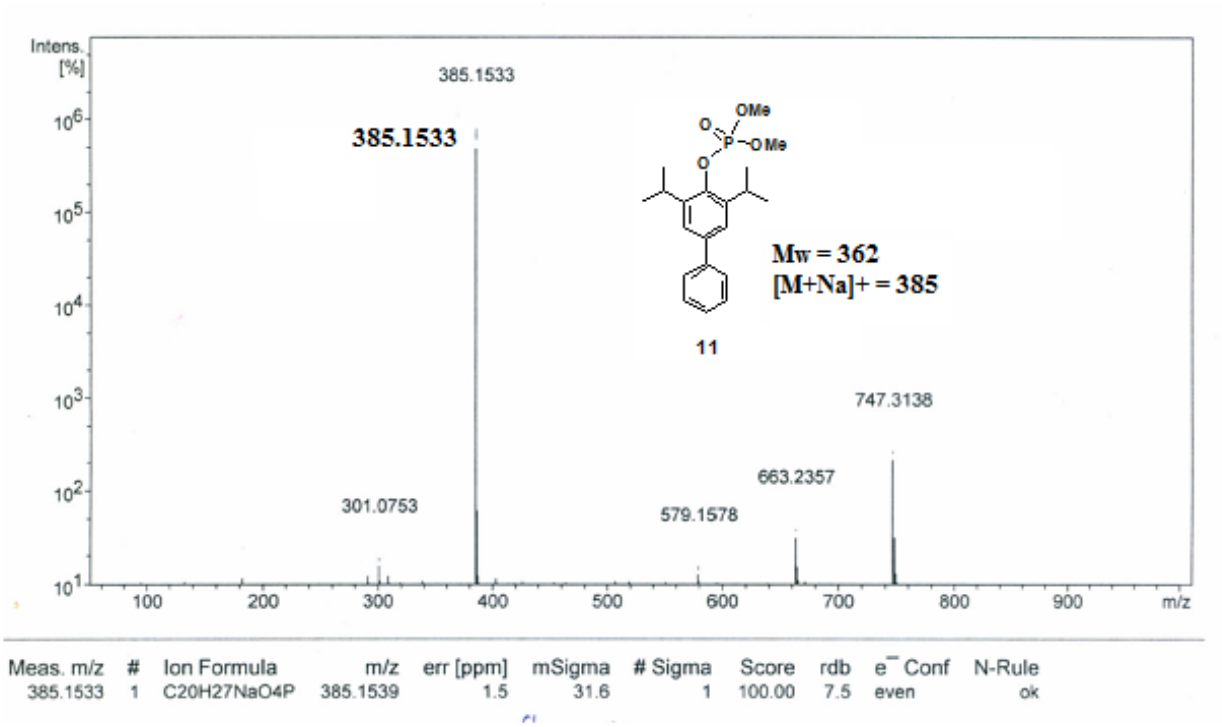


Figure S9. ^{31}P and ^{1}H NMR spectra of compound **5** ($CDCl_3$,, 201 MHz and 500 MHz).



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
385.1533	1	C20H27NaO4P	385.1539	1.5	31.6	1	100.00	7.5	even	ok

Figure S10. ESI-HRMS of compound **5**

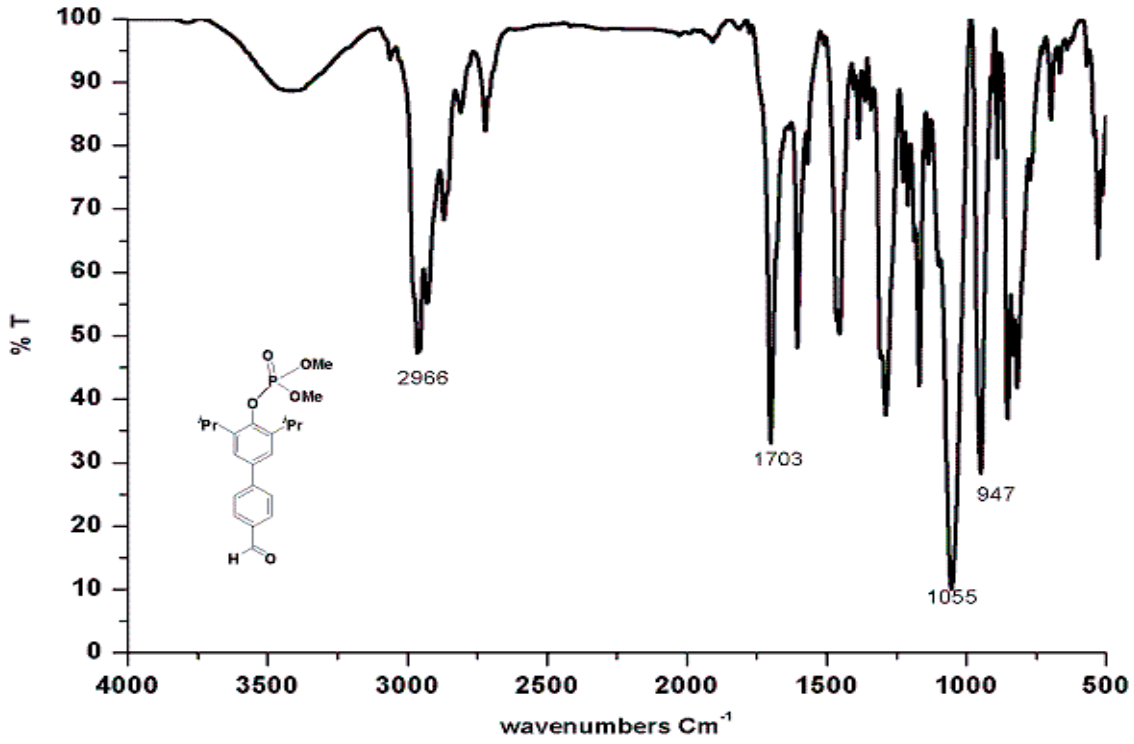


Figure S11. FT-IR spectra of compound **6** (KBr disc)

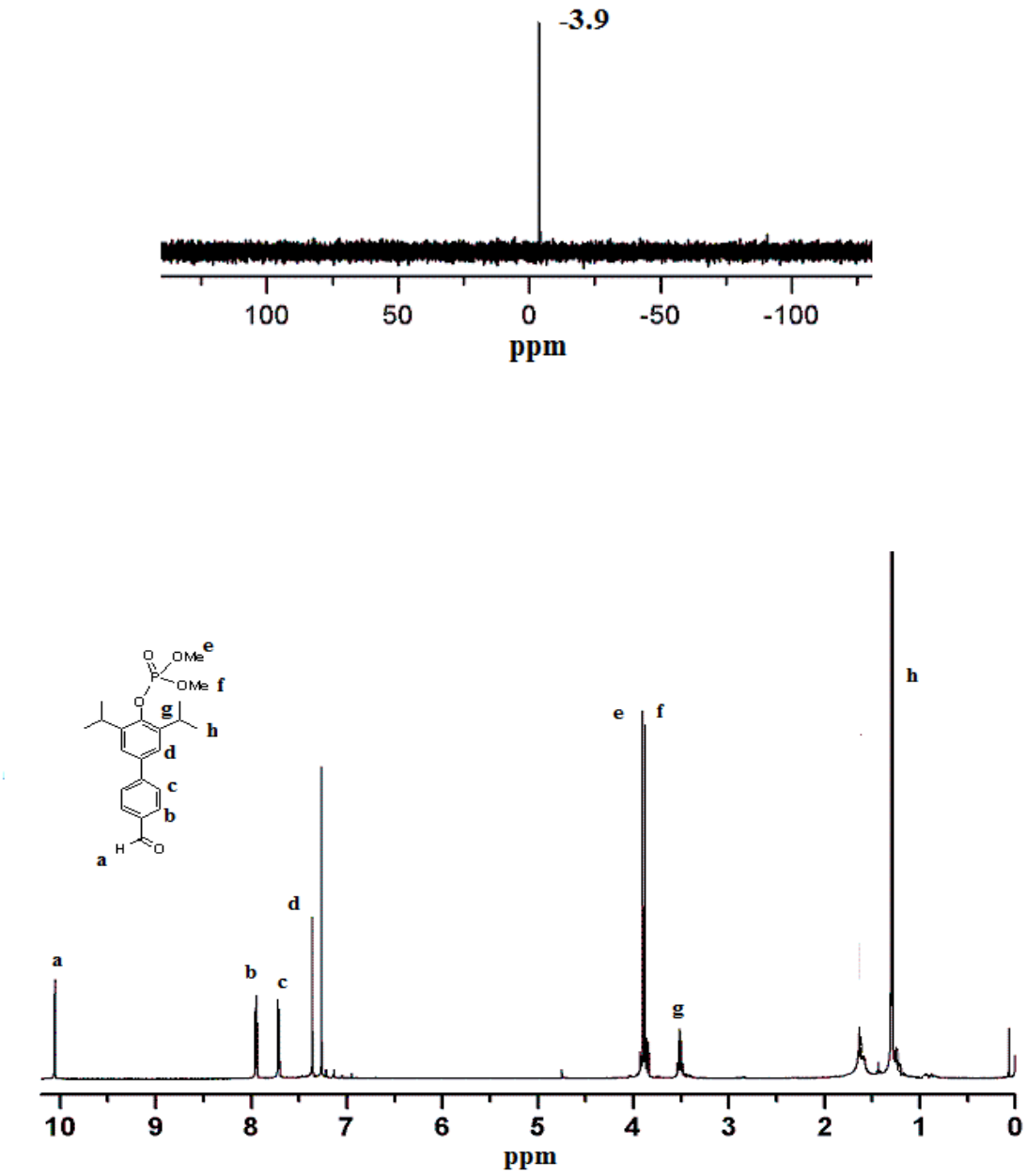


Figure S12. ^{31}P and ^{1}H NMR spectra of compound **6** ($CDCl_3$, 201 MHZ and 500MHz).

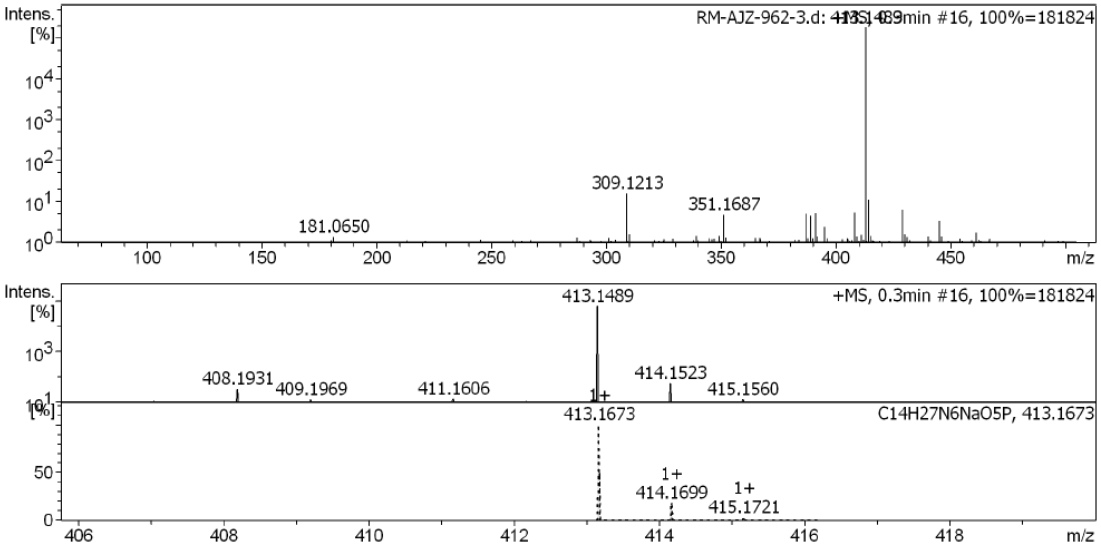
Indian Institute of Technology (B)

Analysis Info

Analysis Name	D:\Data\MARCH-14\RM-AJZ-962-3.d	Acquisition Date	3/31/2014 12:52:14 PM
Method	Tune_pos_Standard_NAI-500.m	Operator	SRK OUT
Sample Name	RM-AJZ-962-3	Instrument	maXis impact 282001.00081
Comment	LRMS		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	500 m/z	Set Collision Cell RF	120.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e¯ Conf	N-Rule
413.1489	1	C21H27NaO5P	413.1488	-0.2	17.8	2	100.00	8.5	even	ok

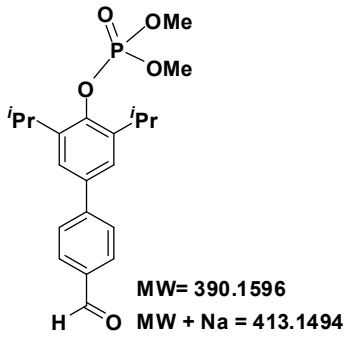


Figure S13. ESI-HRMS of compound **6.**

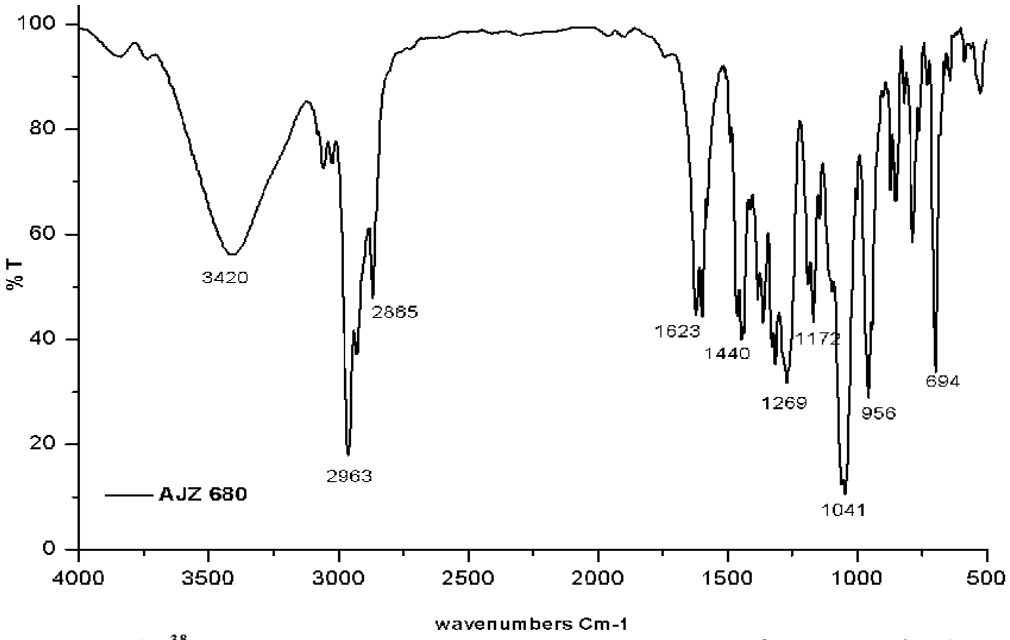
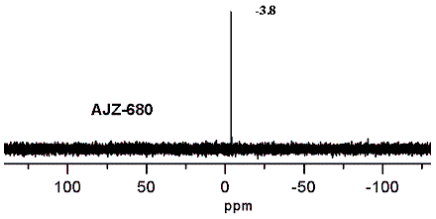


Figure S14. FT-IR spectra of compound **7** (KBr disc)



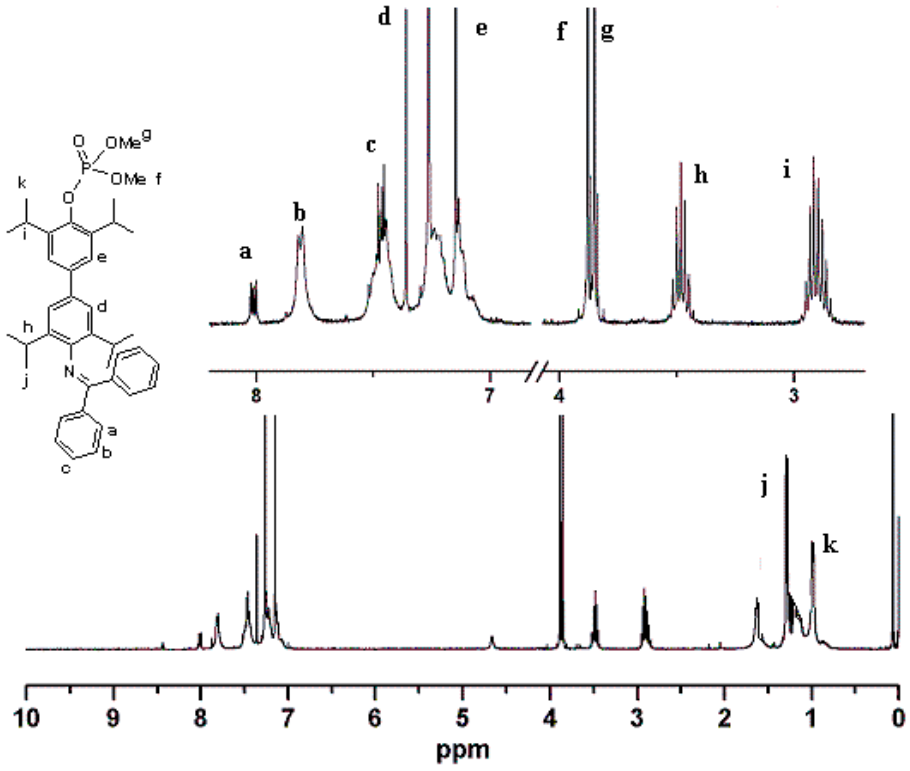


Figure S15. ^{31}P and ^{1}H NMR spectra of compound **7** ($CDCl_3$, 201 MHZ and 500 MHz).

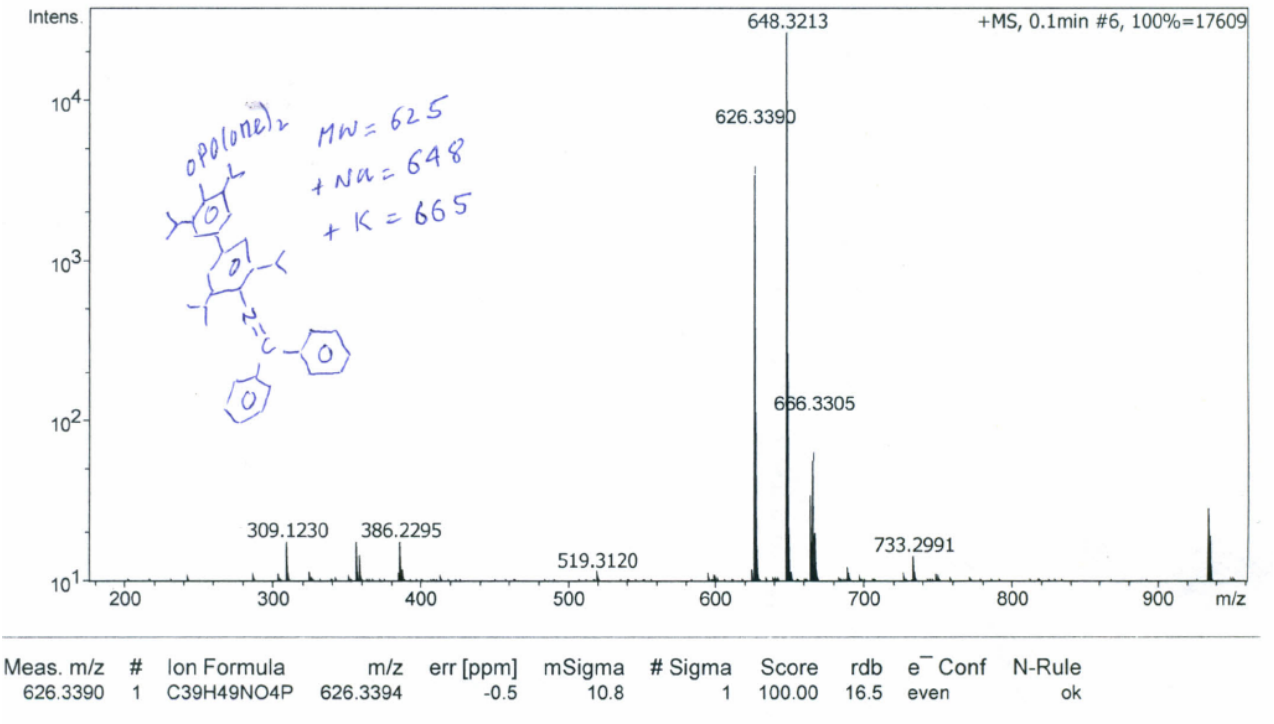


Figure S16. ESI-HRMS of compound **7.**

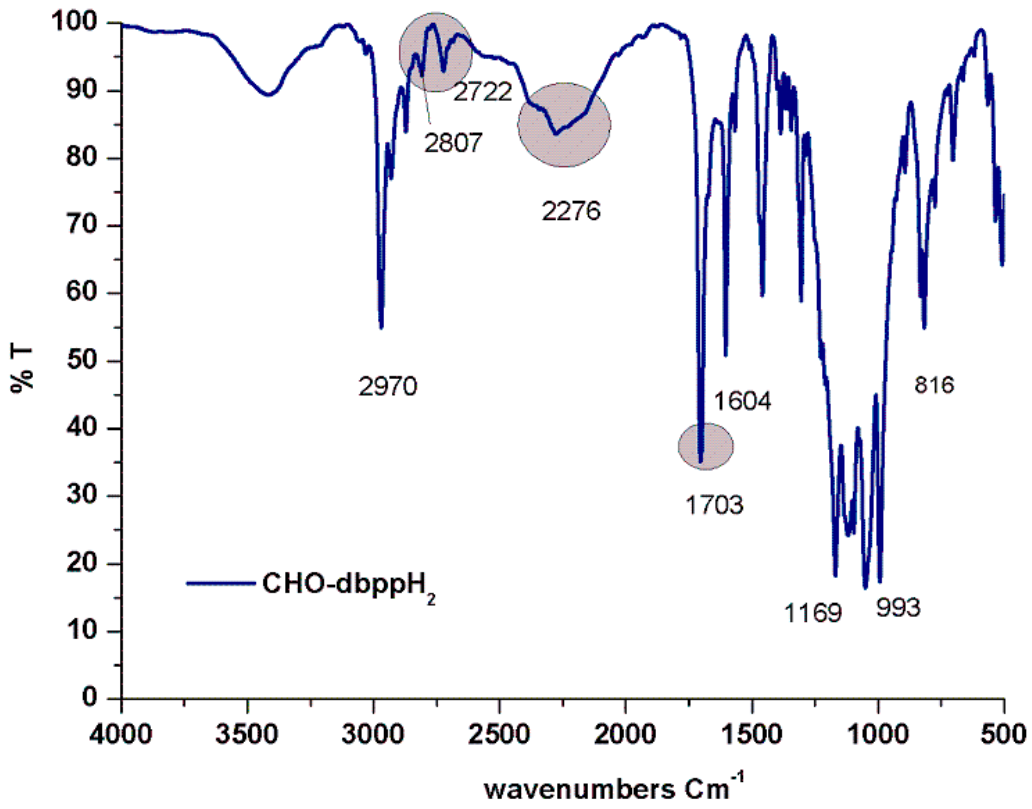


Figure 17. FT-IR spectrum of **8** (KBr disc).

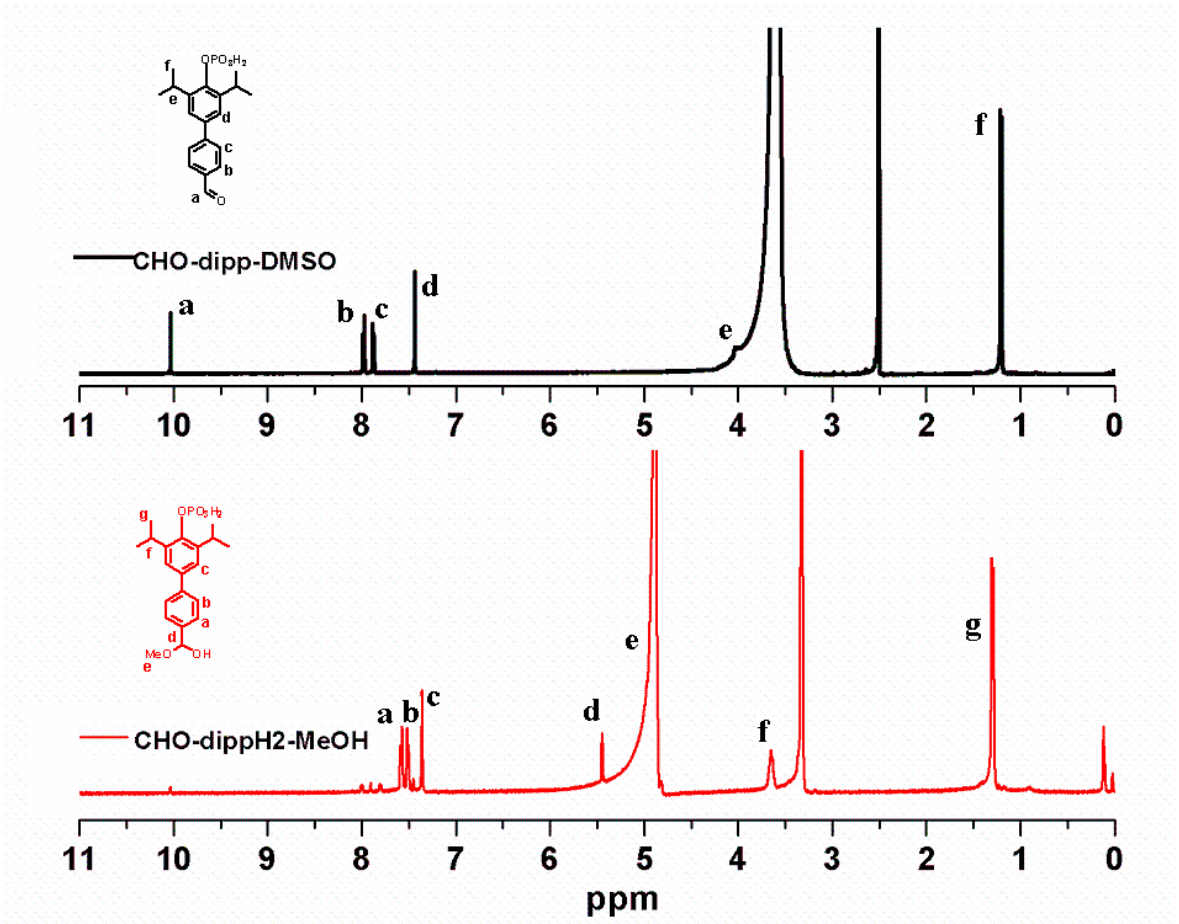


Figure 18. 1HNMR of **8** in DMSO-d_6 (top) and MeOD (bottom). In methanol 14 converts to hemiacetal form.

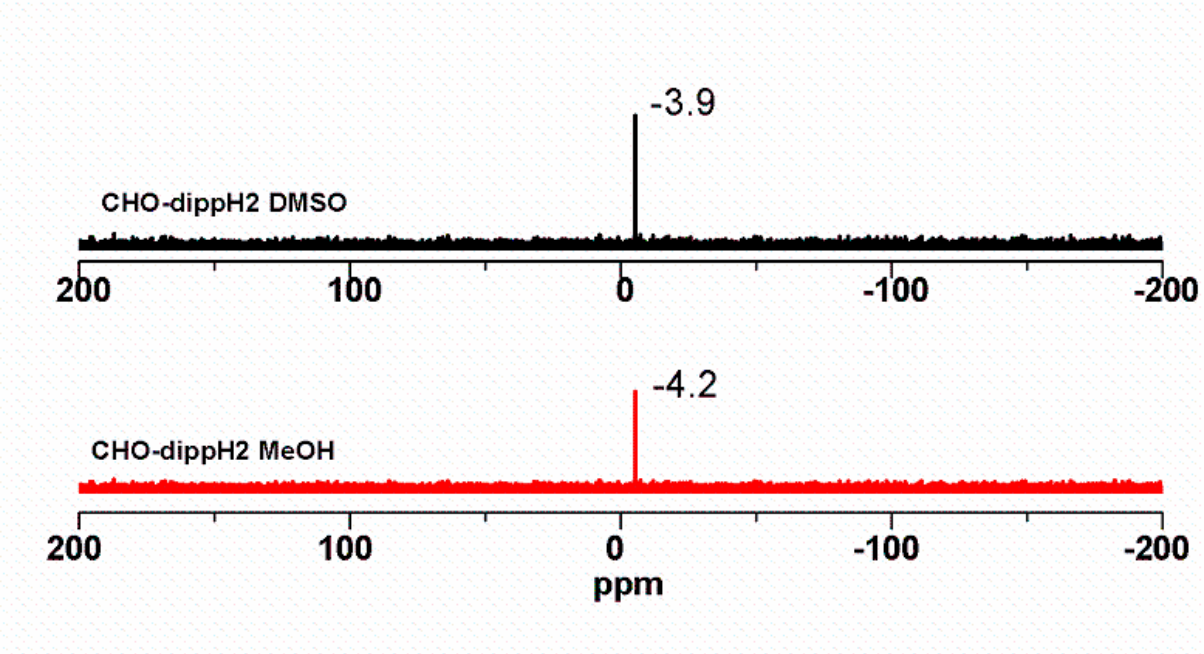


Figure 19. ^{31}P NMR of **8** (DMSO-*d,* and CD_3OD, 125 MHz)

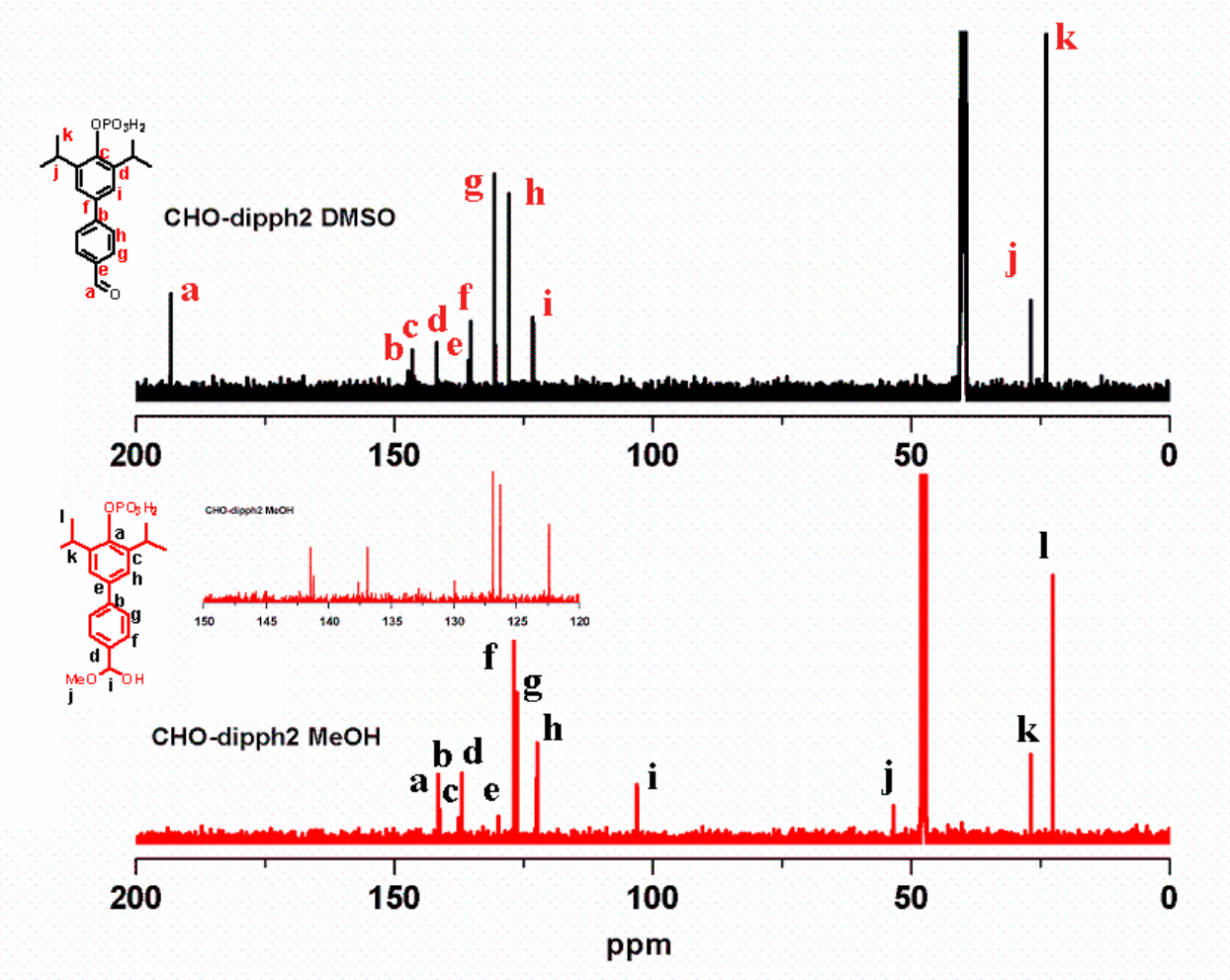


Figure 20 ^{13}C NMR of **14** (DMSO-*d,* and CD_3OD, 125 MHz)

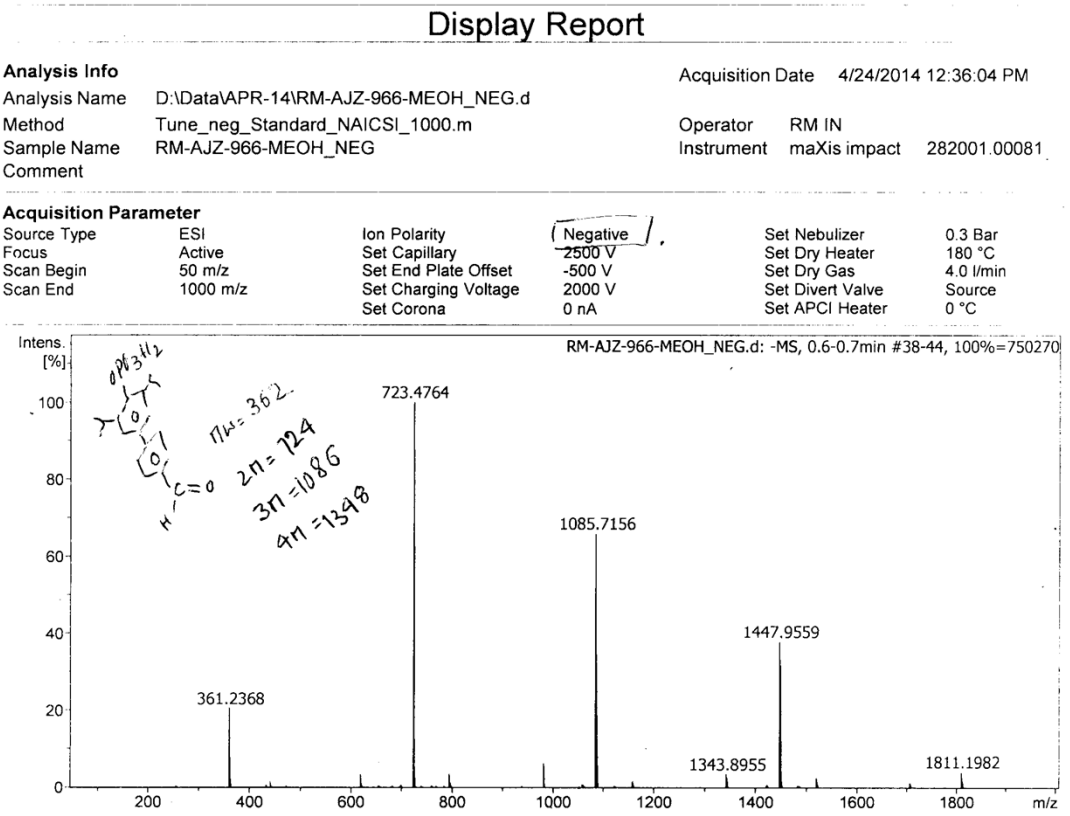
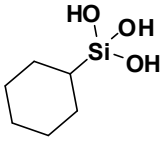
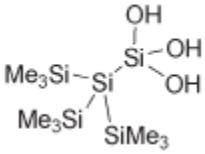
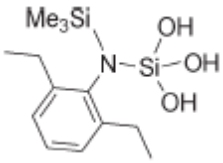
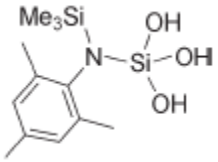
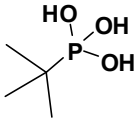
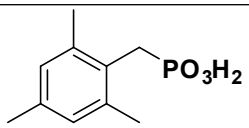
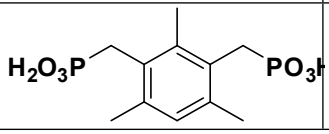
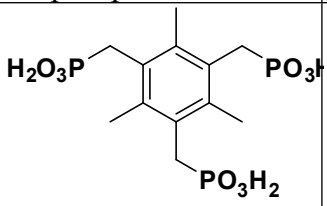
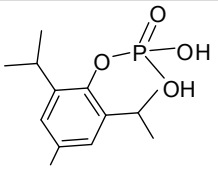
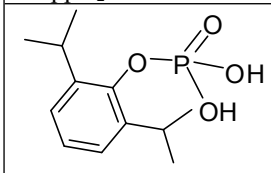
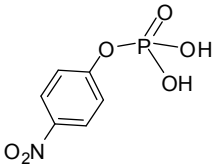
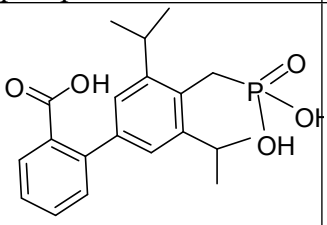
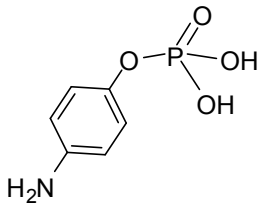


Figure S21. ESI-HRMS (negative mode) of compound **8** (Mw = 362.06)

Table S1. Comparison of H-bonding pattern of compounds with -X-PO_3H_2 functionalities (X = main group element P or Si)

Comparison of H-bonding pattern of compounds with -X-PO_3H_2 functionalities (X = main group element P or Si)			
Compound	**Sp. Group**	**Type of H-bonding**	**Reference**
 cyclohexyl silanetriol	C2/m	**Double-sheet structure** where the –$Si(OH)_3$ groups aggregate in a head-to-head fashion.	H. Ishida, J. L. Koenig and K. C. Gardner, *J. Chem. Phys.,* **1982**, *77*, 5748.
	-	H-bonded **close-shell polyhedral** cluster containing six silanetriol molecules.	S. S. Al-Juaid, N. H. Buttrus, R. I. Damja, Y. Derouiche, C. Eabom, P. B. Hitchcock and P. D. Lickiss, *J. Organomet. Chem*., **1989**, *371*, 287.
	*P*21/c	Forms a **cage structure,** with eight silanetriol molecules in an asymmetric fashion.	G. Prabusankar, R. Murugavel and R. J. Butcher, *Organometallics*, **2005**, *24*, 2124
	Triclinic *P*-1	**Tubular well** structure where the $Si(OH)_3$ moieties come together in a long tubular fashion	R. Murugavel, V. Chandrasekhar, A. Voigt, H. W. Roesky, H. G. Schmidt and M. Noltemeyer, *Organometallics,* **1995**, *14*, 5298.
 tert-butylphosphonic acid	Monoclinic C2c	Two different types of aggregates depending on the solvent of the crystallisation (**H-bonded polymer from THF and discrete hexameric cluster from $CDCl_3$**).	M. Mehring, M. Schürmann and R. Ludwig, *Chem.–Eur. J.*, **2003**, *9*, 837.
 Mono phosphonic acids	Monoclinic *P*2/c	**Ribbon like structure** arranged in head to head manner, -PO3H2 groups lock like zip.	R. Murugavel and M. P. Singh, *New J. Chem.*, **2010**, *34*, 1846.
	Monoclinic $P2_12_12_1$	**Two dimensional sheet** formed by one-dimensional	R. Murugavel and M. P. Singh, *New J. Chem.*, **2010**, *34*, 1846.

Bis phosphonic acids		wave like dimmers.	
 Tris phosphonic acids	Monoclinic *P*2/c	**Three dimensional framework** structure aided by lattice water molecules	R. Murugavel and M. P. Singh, *New J. Chem.*, **2010**, *34*, 1846.
 adippH$_2$.1/3H$_2$O.MeOH\ adippH$_2$.1/3H$_2$O adippH$_2$.MeOH	Trigonal *P*-3c Monoclinic *C*2/c Triclinic *P*-1	**Drum like structure** involving six –PO$_3$ and six NH$_3$ terminals of ligand, formed on water dimer	A. C. Kalita, K. Sharma, Ramaswamy Murugavel, *CrystEngComm*, **2014**, *16*, 51–55
 2,6-diisopropylphenyl phosphate	Monoclinic $P2_1$	**One dimensional chain** structure with double P-OH···O=P hydrogen bonds	A. Onoda, T. Okamura, H. Yamamoto, N. Ueyama, *Acta Cryst.* **2001**, *E57*, o1022-o1024
 4-nitrophenyl phosphate	Monoclinic *P*21	**One dimensional chain** structure with double P-OH···O=P hydrogen bonds	M. Kuczek, I. Bryndal, Tadeusz Lis, *Cryst. Eng. Comm.,* **2006**, *8*, 150–162
 2'-carboxybiphenyl-4-ylmethyl phosphonate	Triclinic *P*-1	**One dimensional chain** structure with double P-OH···O=P hydrogen bonds, the chains bridged by intermolecular –COOH hydrogen bonds into sheets.	W-Q. Kan, J-F. Ma, Y-Y. Liu, J. Yang, B. Liu, *Cryst. Eng. Comm*. **2012**, *14*, 2268–2277
	Monoclinic *P*21	Exists as the zwitterion $H_3N^+C_6H_4PO_3H^-$. In the crystal, molecules are linked by O—H···O and N—H···O hydrogen-bond bridges, giving a **three-dimensional network** structure.	K. Thiele, C. Wagner, K. Merzweiler, *Acta Cryst.* **2012**, *E68*, o263