Electronic Supplementary Information for

2,6-Dimethylphenol derived H-phosphonate and α-hydroxyphosphonate: Facile synthesis, crystal chemistry, supramolecular association and metal complexation

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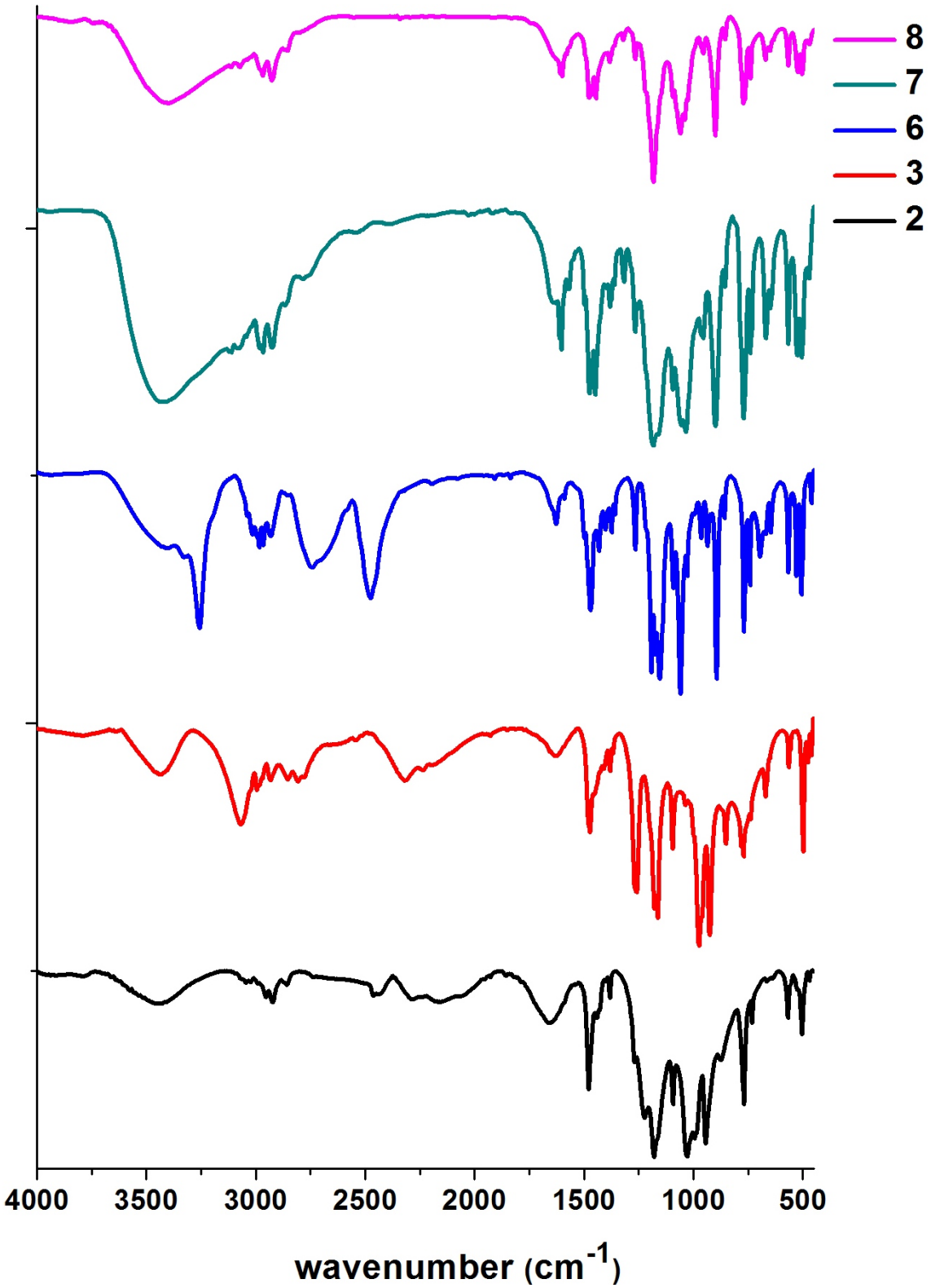


Figure S1. FTIR spectrum of compounds **2-8** as KBr diluted disc.

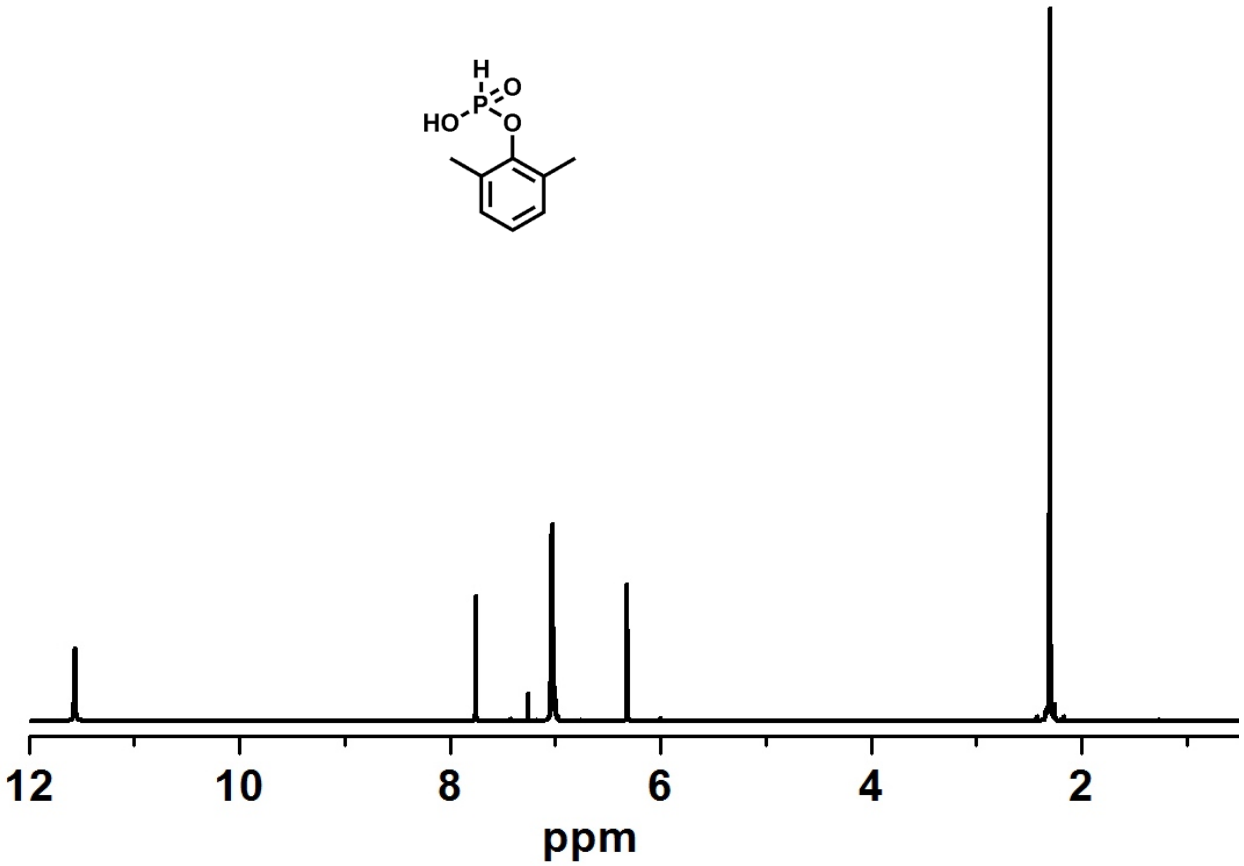


Figure S2. ^{1}H NMR spectrum of compound **2** in $CDCl_3$.

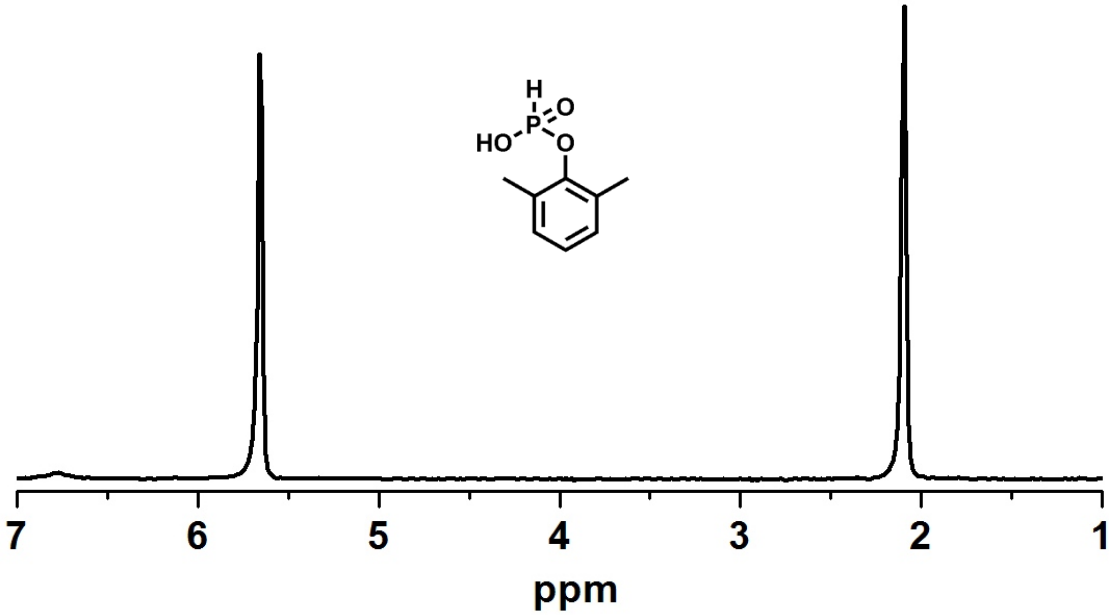


Figure S3. ^{31}P NMR spectrum of compound **2** in $CDCl_3$.

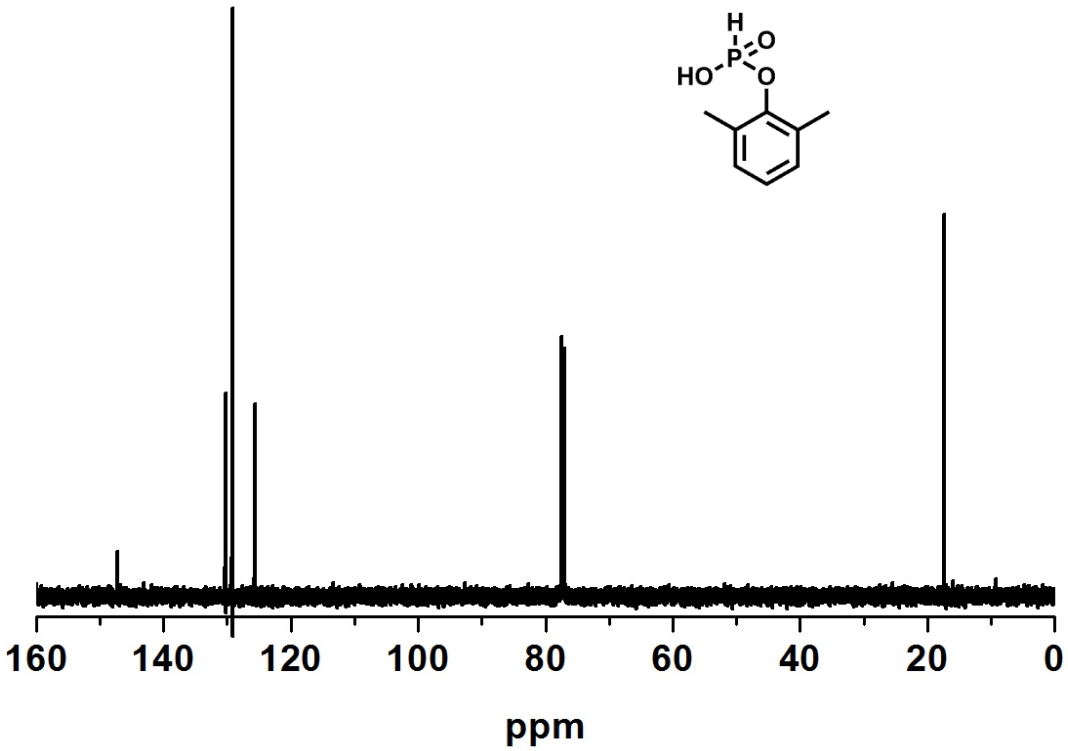
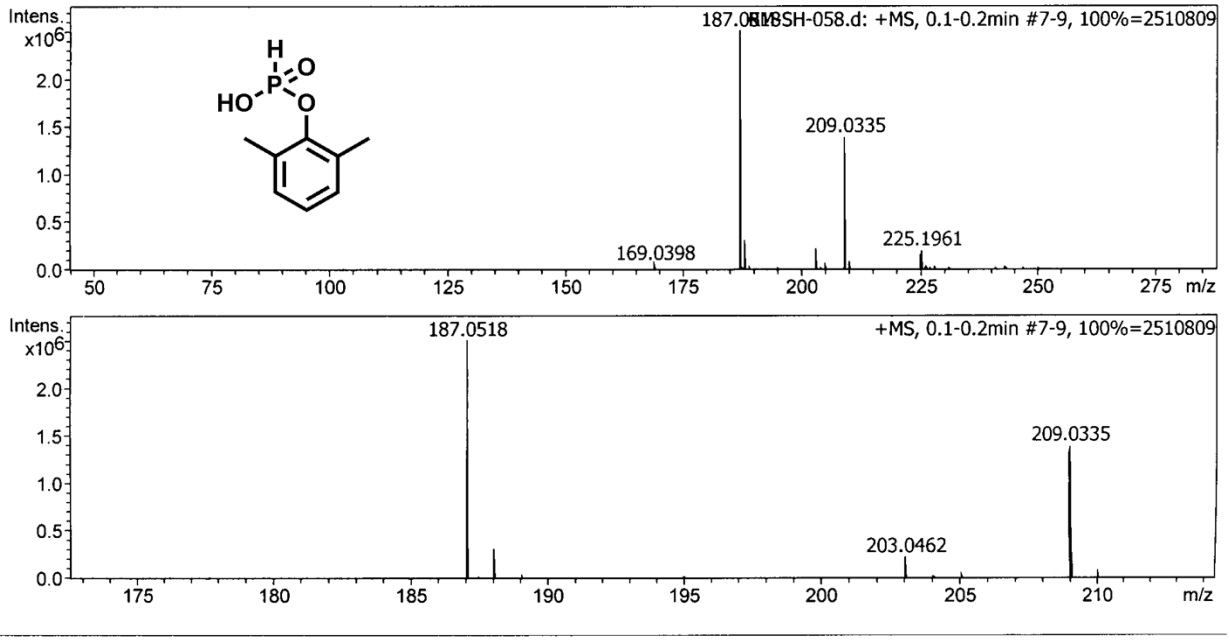


Figure S4. ^{13}C NMR spectrum of compound **2** in $CDCl_3$.



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e⁻ Conf	N-Rule
187.0518	1	C8H12O3P	187.0519	0.4	20.7	1	100.00	3.5	even	ok
209.0335	1	C8H11NaO3P	209.0338	1.3	14.8	1	100.00	3.5	even	ok

Figure S5. ESI-HRMS of compound **2**.

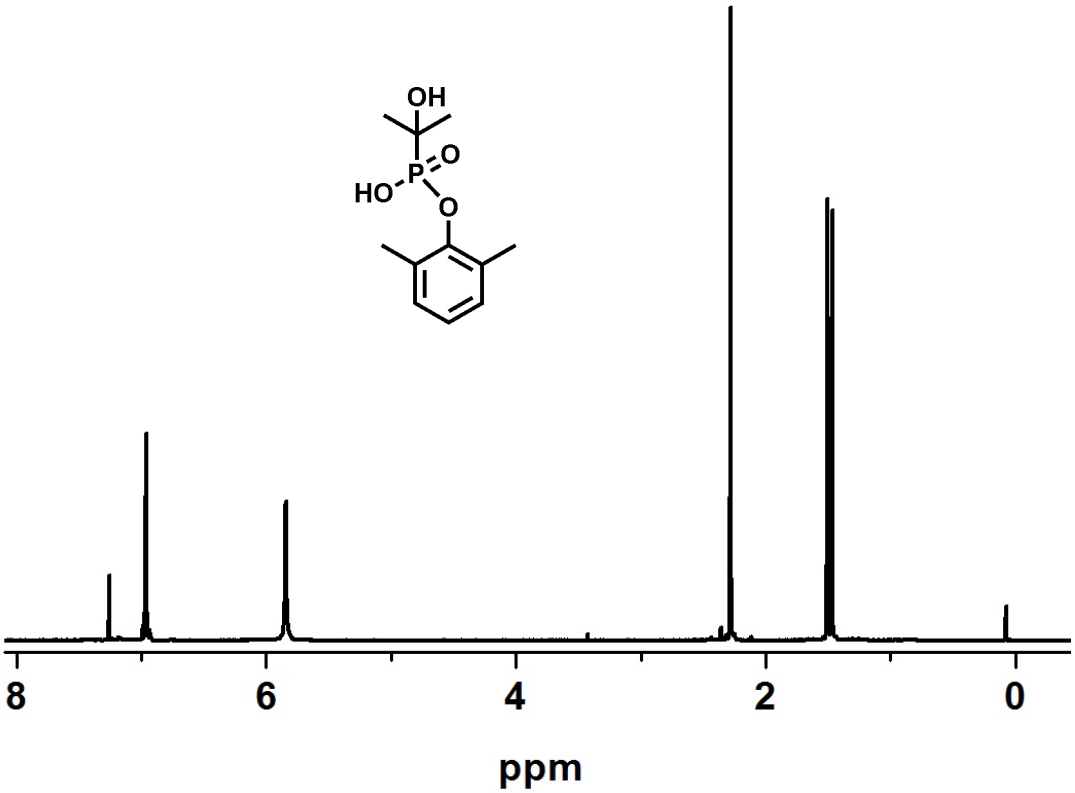


Figure S6. ^{1}H NMR spectrum of compound **3** in $CDCl_3$.

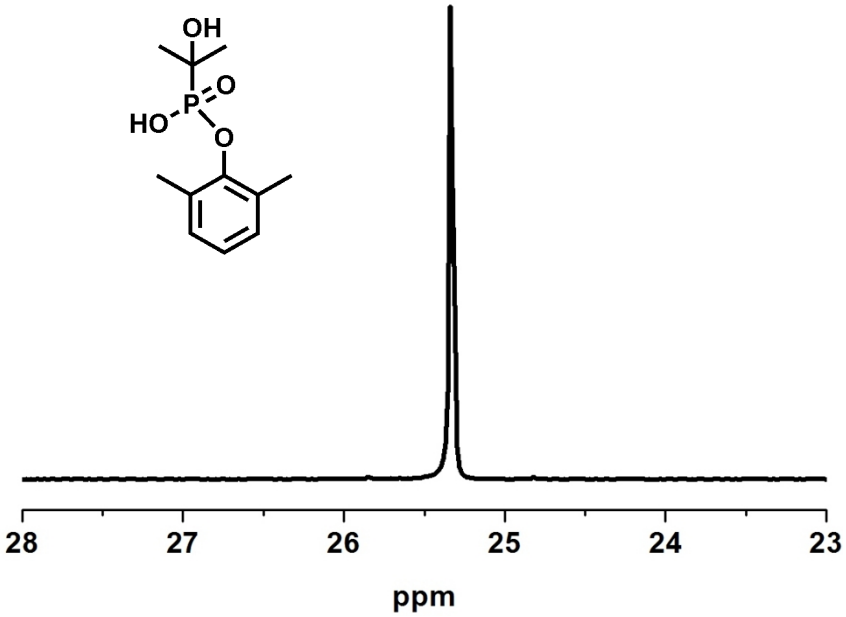


Figure S7. ^{31}P NMR spectrum of compound **3** in $CDCl_3$.

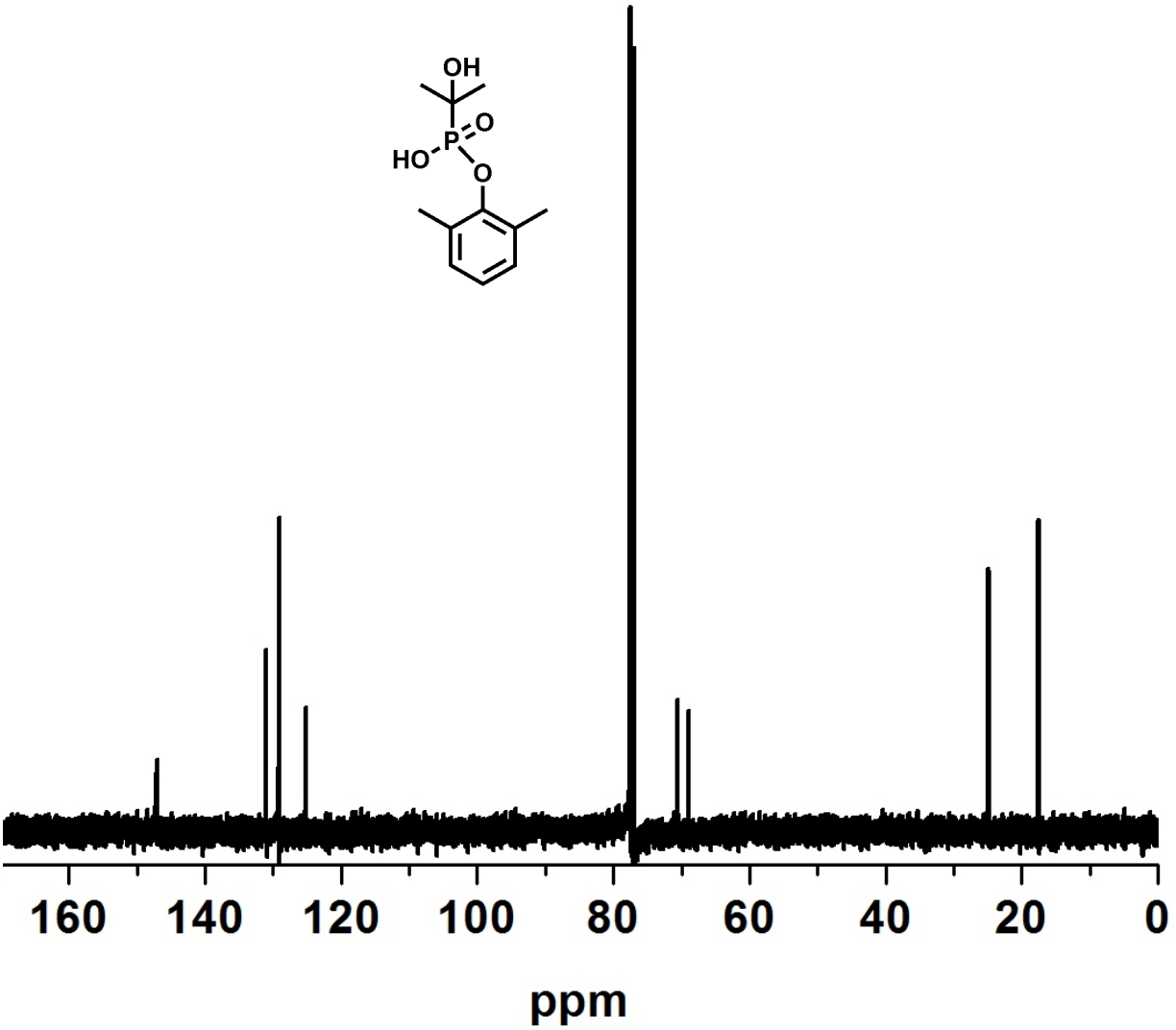


Figure S8. ^{13}C NMR spectrum of compound **3** in $CDCl_3$.

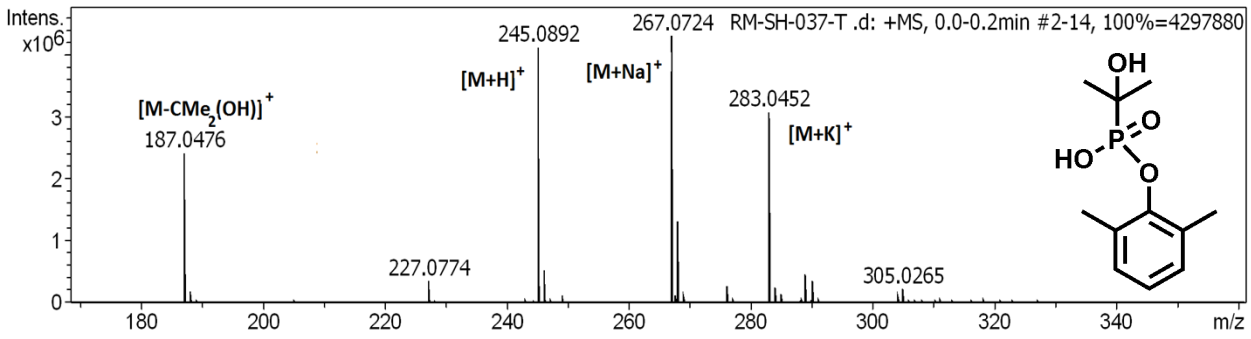


Figure S9. ESI-MS of compound **3** in $CDCl_3$.

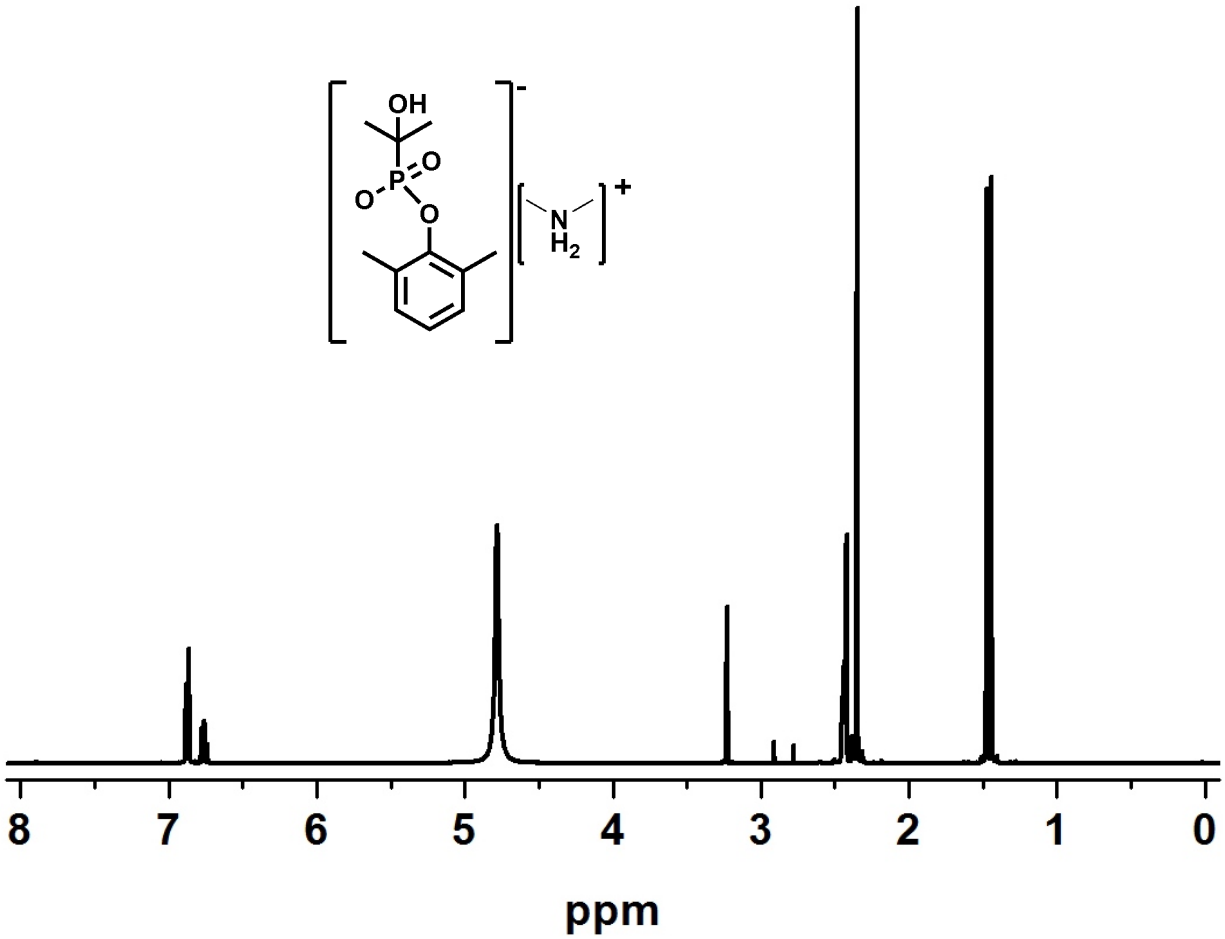


Figure S10. ^{1}H NMR spectrum of compound **6** in CD3OD.

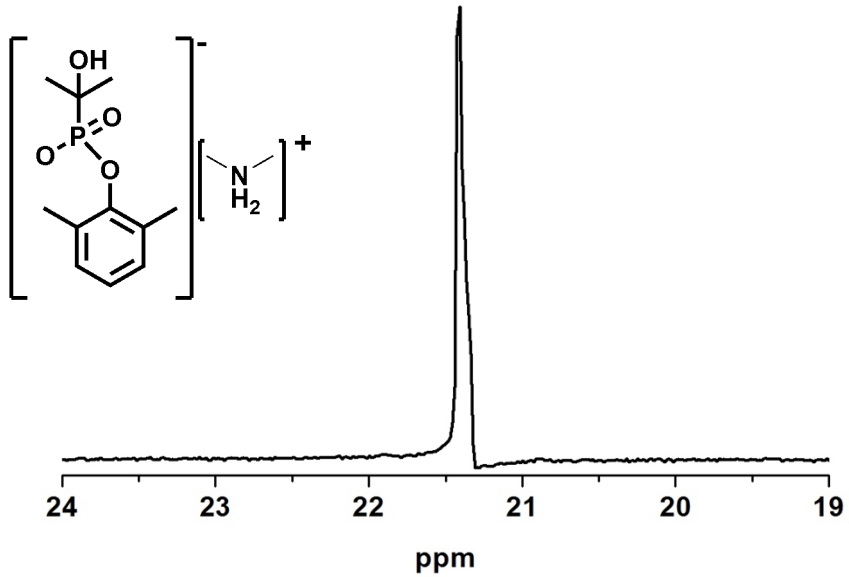


Figure S11. ^{31}P NMR spectrum of compound **6** in CD_3OD.

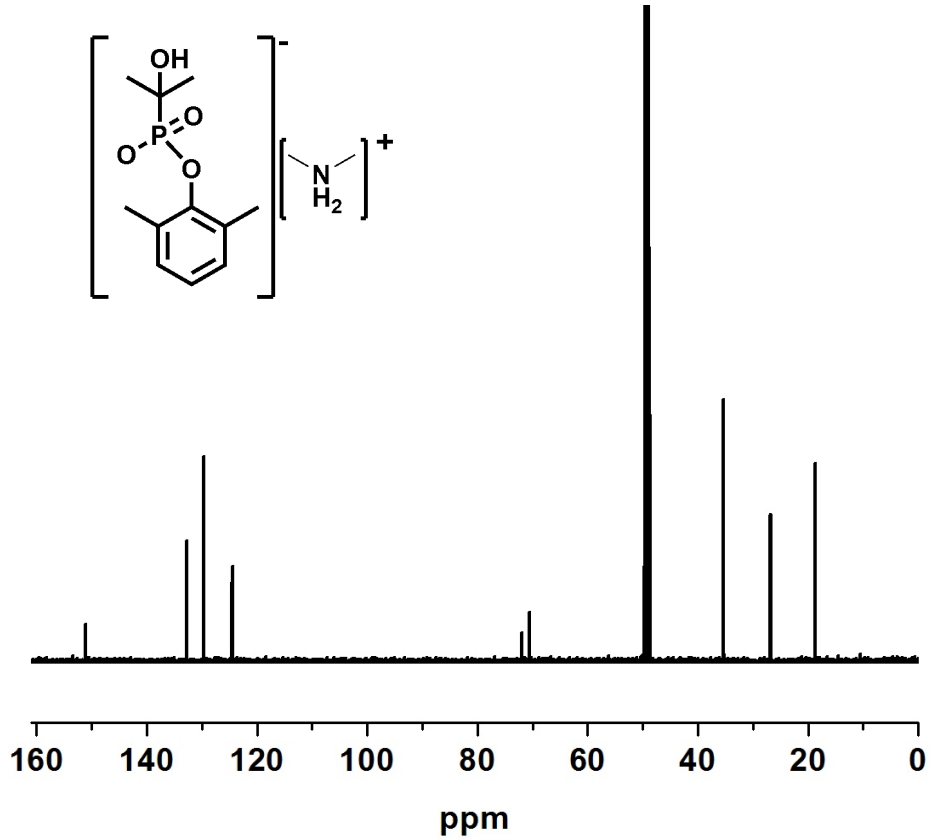


Figure S12. ^{13}C NMR spectrum of compound **6** in CD_3OD.

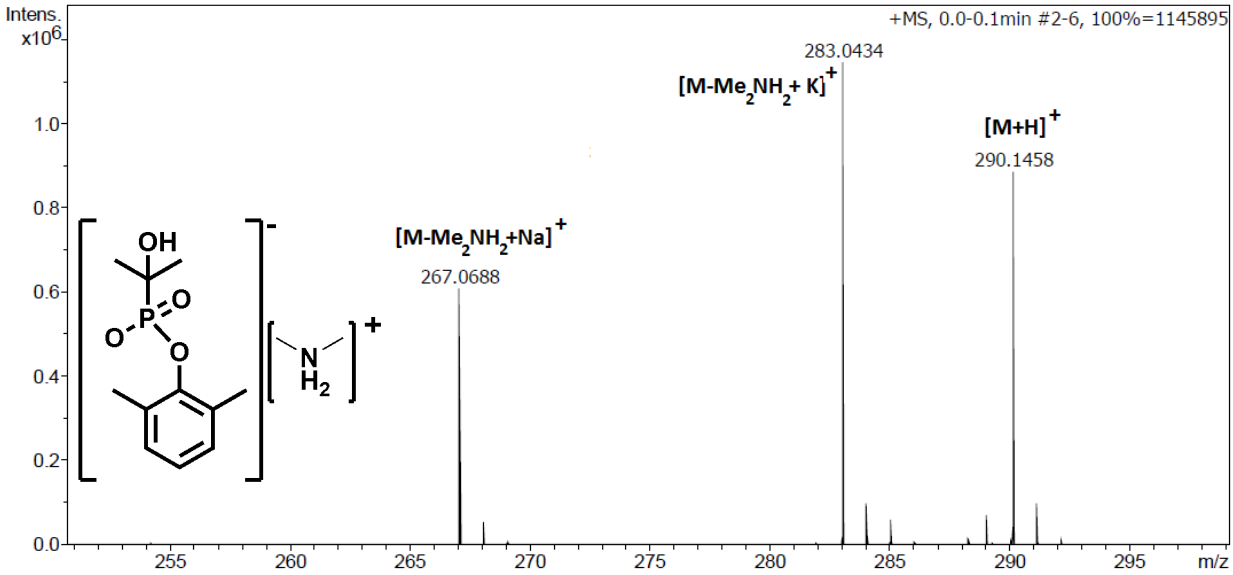


Figure S13. ESI-MS of compound **6** in CD_3OD.

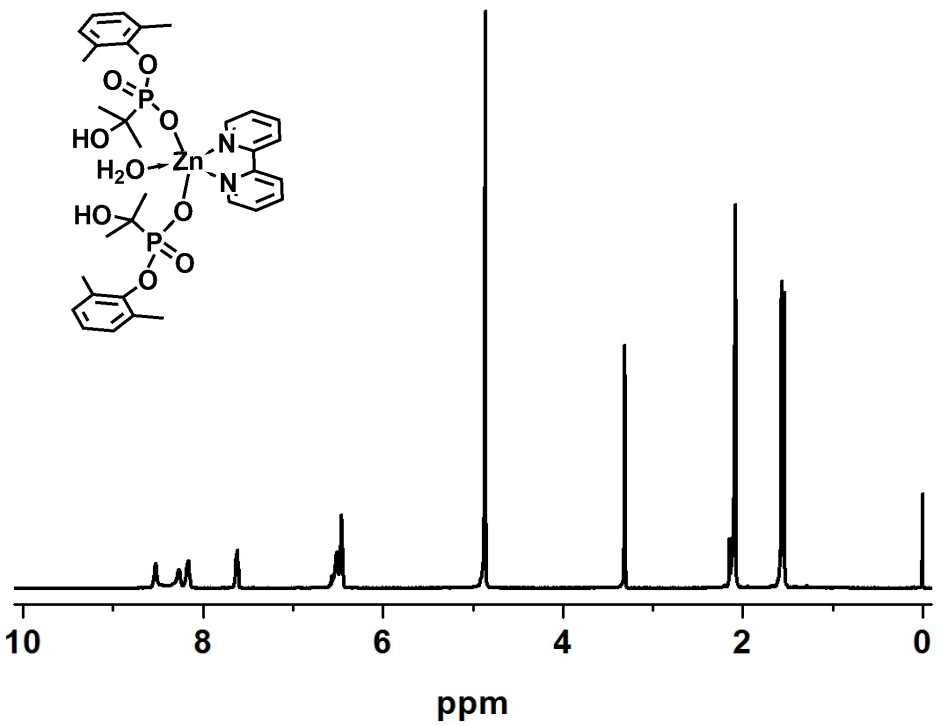


Figure S14. ^{1}H NMR spectrum of compound **8** in CD_3OD.

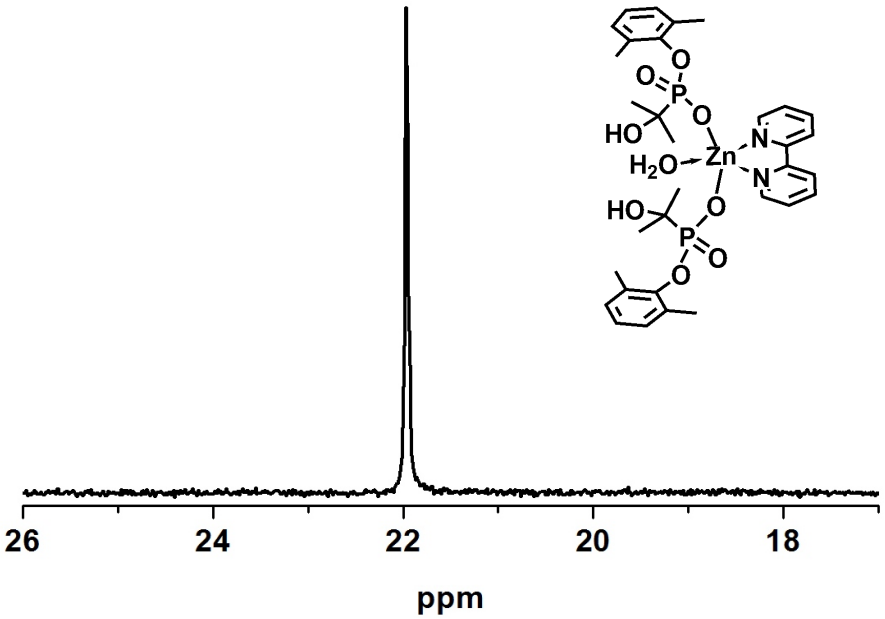


Figure S15. ^{31}P NMR spectrum of compound **8** in CD_3OD.

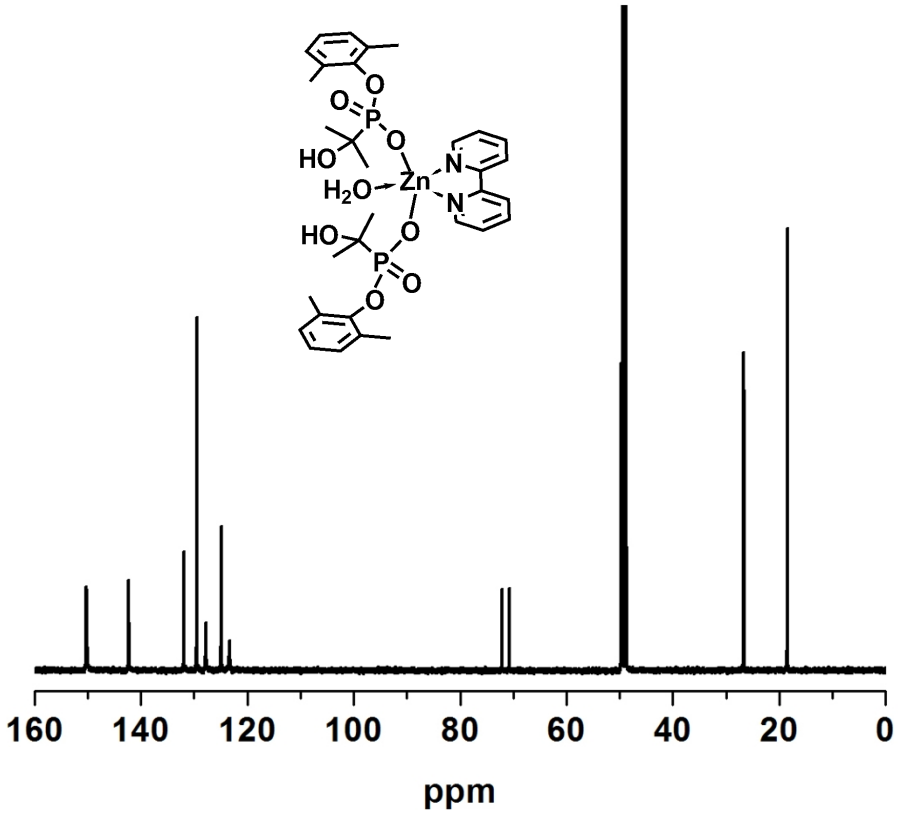


Figure S16. ^{13}C NMR spectrum of compound **8** in CD_3OD.

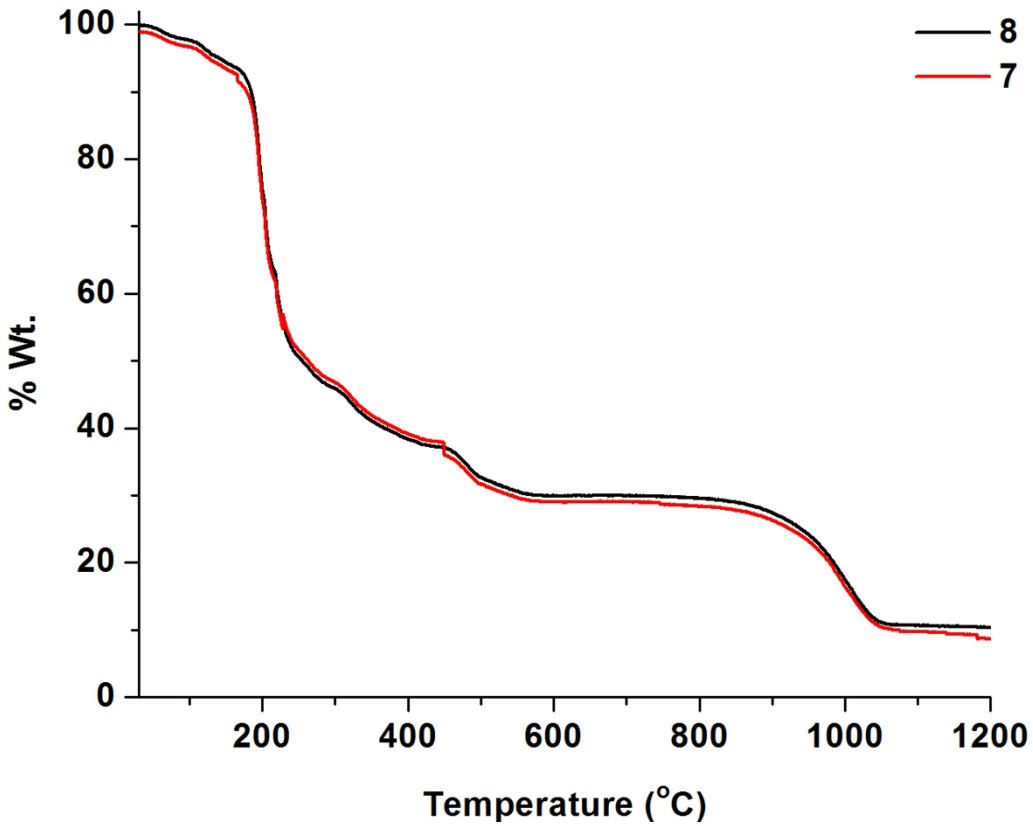


Figure S17. TGA profile of compound **7** and **8**at a heating rate of 10 °C/min.

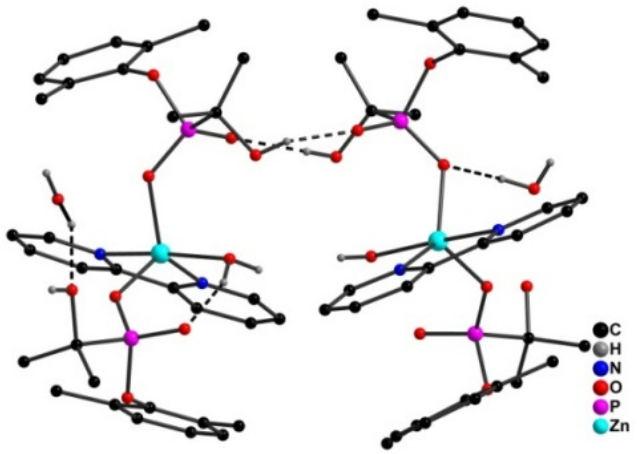


Figure S18. Asymmetric unit of the isomorphous zinc complex **8** (some hydrogen atoms are omitted for clarity).

Table S1. Selected bond distances (Å) and bond angles (°) in **2**.

O(1)-P(1)	1.5790(17)	O(3)-P(1)-O(2)	113.30(13)
O(2)-P(1)	1.527(2)	O(3)-P(1)-O(1)	114.94(10)
O(3)-P(1)	1.469(2)	O(2)-P(1)-O(1)	106.23(11)
P(1)-H(1)	1.28(2)	O(3)-P(1)-H(1)	112.6(11)
C(1)-O(1)-P(1)	126.23(16)	O(2)-P(1)-H(1)	106.6(11)
P(1)-O(2)-H(2)	121(3)	O(1)-P(1)-H(1)	102.2(10)

Table S2. Selected bond distances (Å) and bond angles (°) in **3**.

P(1)-O(1)	1.4702(13)	O(2)-P(1)-O(3)	107.63(7)
P(1)-O(2)	1.5575(13)	O(1)-P(1)-C(9)	115.73(8)
P(1)-O(3)	1.5932(13)	O(2)-P(1)-C(9)	103.27(8)
P(1)-C(9)	1.8274(18)	O(3)-P(1)-C(9)	102.28(7)
O(1)-P(1)-O(2)	114.31(8)	P(1)-O(2)-H(2)	114(2)
O(1)-P(1)-O(3)	112.47(7)	C(1)-O(3)-P(1)	122.05(11)

Table S3. Selected bond distances (Å) and bond angles (°) in **4**.

P(1)-O(1)	1.4883(10)	O(2)-P(1)-O(3)	105.39(5)
P(1)-O(2)	1.5494(10)	O(1)-P(1)-C(9)	113.23(6)
P(1)-O(3)	1.5915(10)	O(2)-P(1)-C(9)	108.39(6)
P(1)-C(9)	1.8226(14)	O(3)-P(1)-C(9)	102.16(6)
O(1)-P(1)-O(2)	113.20(6)	P(1)-O(2)-H(2)	116.2(14)
O(1)-P(1)-O(3)	113.61(5)	C(1)-O(3)-P(1)	122.66(8)

Table S4. Selected bond distances (Å) and bond angles (°) in **5**.

C(9)-P(1)	1.815(3)	O(11)-P(3)	1.470(2)	O(6)-P(2)-O(5)	107.71(11)
C(20)-P(2)	1.821(3)	C(1)-O(1)-P(1)	121.13(17)	O(7)-P(2)-C(20)	114.33(11)
C(31)-P(3)	1.824(3)	O(3)-P(1)-O(2)	113.96(16)	O(6)-P(2)-C(20)	107.25(13)
O(1)-P(1)	1.5945(19)	O(3)-P(1)-O(1)	111.47(13)	O(5)-P(2)-C(20)	100.23(11)
O(2)-P(1)	1.518(2)	O(2)-P(1)-O(1)	107.10(11)	C(23)-O(9)-P(3)	123.25(16)
O(3)-P(1)	1.474(2)	O(3)-P(1)-C(9)	111.52(13)	O(11)-P(3)-O(10)	113.39(11)
O(5)-P(2)	1.5999(19)	O(2)-P(1)-C(9)	109.79(13)	O(11)-P(3)-O(9)	114.08(11)
O(6)-P(2)	1.523(2)	O(1)-P(1)-C(9)	102.27(11)	O(10)-P(3)-O(9)	105.53(11)
O(7)-P(2)	1.4932(18)	C(12)-O(5)-P(2)	122.38(16)	O(11)-P(3)-C(31)	113.70(14)
O(9)-P(3)	1.5982(19)	O(7)-P(2)-O(6)	113.68(11)	O(10)-P(3)-C(31)	108.19(13)
O(10)-P(3)	1.556(2)	O(7)-P(2)-O(5)	112.60(10)	O(9)-P(3)-C(31)	100.92(12)

Table S5. Selected bond distances (Å) and bond angles (°) in **6**.

P(1)-O(3)	1.5016(14)	O(2)-P(1)-C(9)	112.09(8)
P(1)-O(2)	1.5054(13)	O(1)-P(1)-C(9)	97.80(7)
P(1)-O(1)	1.6237(13)	C(1)-O(1)-P(1)	122.80(11)
P(1)-C(9)	1.8315(19)	C(13)-N(1)-C(12)	111.94(16)
N(1)-C(13)	1.481(2)	C(13)-N(1)-H(1A)	110.0(15)
N(1)-C(12)	1.484(2)	C(12)-N(1)-H(1A)	108.1(15)
O(3)-P(1)-O(2)	114.54(8)	C(13)-N(1)-H(1B)	107.5(14)
O(3)-P(1)-O(1)	110.53(7)	C(12)-N(1)-H(1B)	109.2(13)
O(2)-P(1)-O(1)	109.73(7)	H(1A)-N(1)-H(1B)	110(2)
O(3)-P(1)-C(9)	110.90(9)		

Table S6. Selected bond distances (Å) and bond angles (°) in **7**.

Cu(1)-O(17)	1.979(3)	O(17)-Cu(1)-N(1)	174.59(14)	C(34)-O(13)-P(4)	120.0(3)
Cu(1)-N(1)	1.980(4)	O(17)-Cu(1)-N(2)	93.83(13)	P(4)-O(14)-Cu(2)	123.35(17)
Cu(1)-N(2)	2.023(4)	N(1)-Cu(1)-N(2)	80.77(14)	O(3)-P(1)-O(2)	115.75(18)
Cu(1)-O(2)	2.058(3)	O(17)-Cu(1)-O(2)	92.63(12)	O(3)-P(1)-O(1)	112.13(17)
Cu(1)-O(6)	2.073(3)	N(1)-Cu(1)-O(2)	91.33(14)	O(2)-P(1)-O(1)	108.85(16)
Cu(2)-N(4)	1.972(3)	N(2)-Cu(1)-O(2)	133.69(14)	O(3)-P(1)-C(9)	111.36(18)
Cu(2)-O(18)	1.987(3)	O(17)-Cu(1)-O(6)	92.52(12)	O(2)-P(1)-C(9)	108.61(18)
Cu(2)-N(3)	2.018(4)	N(1)-Cu(1)-O(6)	90.37(14)	O(1)-P(1)-C(9)	98.78(18)
Cu(2)-O(10)	2.062(3)	N(2)-Cu(1)-O(6)	124.79(14)	O(7)-P(2)-O(6)	114.61(17)
Cu(2)-O(14)	2.069(3)	O(2)-Cu(1)-O(6)	100.62(12)	O(7)-P(2)-O(5)	111.56(17)
C(9)-P(1)	1.838(4)	N(4)-Cu(2)-O(18)	174.11(14)	O(6)-P(2)-O(5)	109.77(17)
C(20)-P(2)	1.828(5)	N(4)-Cu(2)-N(3)	80.46(14)	O(7)-P(2)-C(20)	112.3(2)
C(31)-P(3)	1.832(5)	O(18)-Cu(2)-N(3)	93.69(13)	O(6)-P(2)-C(20)	109.55(19)
C(42)-P(4)	1.832(4)	N(4)-Cu(2)-O(10)	90.40(13)	O(5)-P(2)-C(20)	97.73(19)
O(1)-P(1)	1.626(3)	O(18)-Cu(2)-O(10)	92.80(12)	O(11)-P(3)-O(10)	115.11(17)
O(2)-P(1)	1.513(3)	N(3)-Cu(2)-O(10)	129.53(14)	O(11)-P(3)-O(9)	111.29(18)
O(3)-P(1)	1.492(3)	N(4)-Cu(2)-O(14)	91.50(14)	O(10)-P(3)-O(9)	108.90(17)
O(5)-P(2)	1.614(3)	O(18)-Cu(2)-O(14)	92.86(12)	O(11)-P(3)-C(31)	111.7(2)
O(6)-P(2)	1.513(3)	N(3)-Cu(2)-O(14)	130.21(14)	O(10)-P(3)-C(31)	110.0(2)
O(7)-P(2)	1.497(3)	O(10)-Cu(2)-O(14)	99.31(12)	O(9)-P(3)-C(31)	98.70(19)
O(9)-P(3)	1.617(3)	C(1)-O(1)-P(1)	122.2(3)	O(15)-P(4)-O(14)	116.33(18)
O(10)-P(3)	1.507(3)	P(1)-O(2)-Cu(1)	122.45(17)	O(15)-P(4)-O(13)	111.47(17)
O(11)-P(3)	1.501(3)	C(12)-O(5)-P(2)	122.0(3)	O(14)-P(4)-O(13)	108.44(16)
O(13)-P(4)	1.623(3)	P(2)-O(6)-Cu(1)	126.68(16)	O(15)-P(4)-C(42)	111.49(18)
O(14)-P(4)	1.515(3)	C(23)-O(9)-P(3)	121.3(3)	O(14)-P(4)-C(42)	108.53(18)
O(15)-P(4)	1.482(3)	P(3)-O(10)-Cu(2)	125.80(16)	O(13)-P(4)-C(42)	99.16(18)

Table S7. Selected bond distances (Å) and bond angles (°) in **8**.

N(1)-Zn(1)	2.130(5)	O(15)-P(4)	1.494(4)	O(3)-P(1)-O(2)	115.4(2)
N(2)-Zn(1)	2.068(5)	O(6)-Zn(1)-O(2)	109.02(18)	O(3)-P(1)-O(1)	112.1(2)
O(2)-Zn(1)	1.988(4)	O(6)-Zn(1)-N(2)	122.30(19)	O(2)-P(1)-O(1)	108.2(2)
O(6)-Zn(1)	1.975(4)	O(2)-Zn(1)-N(2)	127.87(18)	O(3)-P(1)-C(9)	112.0(3)
O(17)-Zn(1)	2.117(4)	O(6)-Zn(1)-O(17)	92.51(17)	O(2)-P(1)-C(9)	108.8(3)
N(3)-Zn(2)	2.075(5)	O(2)-Zn(1)-O(17)	92.12(17)	O(1)-P(1)-C(9)	99.1(3)
N(4)-Zn(2)	2.112(5)	N(2)-Zn(1)-O(17)	94.05(18)	O(7)-P(2)-O(6)	115.2(2)
O(10)-Zn(2)	1.981(4)	O(6)-Zn(1)-N(1)	92.08(19)	O(7)-P(2)-O(5)	112.3(3)
O(14)-Zn(2)	1.974(4)	O(2)-Zn(1)-N(1)	92.88(19)	O(6)-P(2)-O(5)	108.5(2)
O(18)-Zn(2)	2.126(4)	N(2)-Zn(1)-N(1)	77.7(2)	O(7)-P(2)-C(20)	111.9(3)
C(9)-P(1)	1.842(6)	O(17)-Zn(1)-N(1)	171.72(18)	O(6)-P(2)-C(20)	109.1(3)
C(20)-P(2)	1.820(7)	O(14)-Zn(2)-O(10)	107.06(18)	O(5)-P(2)-C(20)	98.5(3)
C(41)-P(3)	1.827(6)	O(14)-Zn(2)-N(3)	125.60(19)	O(12)-P(3)-O(10)	115.1(3)
C(52)-P(4)	1.826(6)	O(10)-Zn(2)-N(3)	126.51(19)	O(12)-P(3)-O(9)	112.3(2)
O(1)-P(1)	1.616(4)	O(14)-Zn(2)-N(4)	91.6(2)	O(10)-P(3)-O(9)	107.6(2)
O(2)-P(1)	1.521(4)	O(10)-Zn(2)-N(4)	93.39(19)	O(12)-P(3)-C(41)	112.3(3)
O(3)-P(1)	1.495(4)	N(3)-Zn(2)-N(4)	77.7(2)	O(10)-P(3)-C(41)	108.9(3)
O(5)-P(2)	1.618(5)	O(14)-Zn(2)-O(18)	92.95(17)	O(9)-P(3)-C(41)	99.4(3)
O(6)-P(2)	1.510(5)	O(10)-Zn(2)-O(18)	92.73(17)	O(15)-P(4)-O(14)	115.3(3)
O(7)-P(2)	1.503(5)	N(3)-Zn(2)-O(18)	93.29(19)	O(15)-P(4)-O(13)	111.8(3)
O(9)-P(3)	1.623(4)	N(4)-Zn(2)-O(18)	170.96(19)	O(14)-P(4)-O(13)	108.4(2)
O(10)-P(3)	1.525(4)	C(1)-O(1)-P(1)	123.5(4)	O(15)-P(4)-C(52)	112.0(3)
O(12)-P(3)	1.484(4)	C(12)-O(5)-P(2)	122.1(4)	O(14)-P(4)-C(52)	109.1(3)
O(13)-P(4)	1.617(5)	C(33)-O(9)-P(3)	121.2(4)	O(13)-P(4)-C(52)	98.9(3)
O(14)-P(4)	1.519(5)	C(44)-O(13)-P(4)	120.7(4)		