Electronic Supplementary Information

Coordination *versus* spodium bonds in the dinuclear Zn(II) and Cd(II) complexes with a dithiophosphate ligand

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Table S1 Selected bond lengths (angstroms) of complexes **1** and **2**

Complex 1		**Complex 2**	
Zn1—S4^{i}	2.3394 (10)	Cd1—S4	3.003 (3)
Zn1—S2	2.4321 (11)	Cd1—S4^{ii}	2.584 (3)
Zn1—S3	2.3146 (11)	Cd1—S1	2.602 (3)
Zn1—S1	2.3578 (12)	Cd1—S2	2.582 (3)
S4—Zn1^{i}	2.3394 (10)	Cd1—S3	2.590 (3)
S4—P2	1.9869 (14)	S4—P2	2.020 (3)
P2—S3	1.9971 (15)	S1—P1	1.982 (4)
P2—O4	1.596 (3)	P1—S2	1.983 (4)
P2—O3	1.588 (3)	P1—O1	1.592 (6)

S2—P1	1.9791 (15)	P1—O2	1.594 (7)
P1—S1	1.9895 (15)	P2—S3	1.975 (4)
P1—O1	1.584 (3)	P2—O4	1.583 (7)
P1—O2	1.596 (3)	P2—O3	1.579 (7)
O4—C31	1.415 (4)	O1—C1	1.401 (11)
O1—C1	1.407 (5)	O4—C31	1.431 (11)
O3—C21	1.422 (5)	O3—C21	1.415 (11)
O2—C11	1.410 (5)	O2—C11	1.410 (11)

Symmetry code(s): (i) −*x*+1, *y*, −*z*+3/2; (ii) −*x*+1, −*y*+1, −*z*+1.

Table S2 Selected bond angles (degrees) of complexes **1** and **2**

Complex 1		**Complex 2**	
$S4^{i}$—Zn1—S2	105.95 (4)	$S4^{ii}$—Cd1—S4	86.47 (8)
$S4^{i}$—Zn1—P1	112.53 (4)	$S4^{ii}$—Cd1—S1	104.61 (8)
$S4^{i}$—Zn1—S1	111.76 (4)	$S4^{ii}$—Cd1—P1	137.63 (8)
S2—Zn1—P1	43.10 (3)	S4—Cd1—P1	127.40 (7)
S3—Zn1—$S4^{i}$	120.39 (4)	$S4^{ii}$—Cd1—S3	103.13 (9)
S3—Zn1—S2	112.70 (4)	S1—Cd1—S4	167.60 (8)
S3—Zn1—P1	126.83 (4)	S1—Cd1—P1	40.20 (8)
S3—Zn1—S1	114.16 (4)	S2—Cd1—$S4^{ii}$	145.16 (9)

S1—Zn1—S2	86.48 (4)	S2—Cd1—S4	87.59 (8)
S1—Zn1—P1	43.64 (3)	S2—Cd1—S1	80.13 (8)
P2—S4—Zn1^{i}	101.78 (5)	S2—Cd1—P1	40.27 (8)
S4—P2—S3	117.56 (7)	S2—Cd1—S3	108.10 (9)
O4—P2—S4	109.06 (12)	S3—Cd1—S4	73.99 (8)
O4—P2—S3	109.47 (11)	S3—Cd1—S1	108.12 (9)
O3—P2—S4	108.14 (11)	S3—Cd1—P1	109.89 (8)
O3—P2—S3	110.82 (13)	Cd1^{ii}—S4—Cd1	93.53 (8)
O3—P2—O4	100.41 (15)	P2—S4—Cd1^{ii}	93.48 (11)
P1—S2—Zn1	79.80 (5)	P2—S4—Cd1	77.44 (10)
P2—S3—Zn1	99.34 (5)	P1—S1—Cd1	81.89 (11)
S2—P1—S1	111.56 (6)	S1—P1—Cd1	57.91 (10)
O1—P1—S2	108.26 (12)	S1—P1—S2	114.61 (16)
O1—P1—S1	112.94 (12)	S2—P1—Cd1	57.35 (10)
O1—P1—O2	99.04 (15)	O1—P1—Cd1	136.9 (3)
O2—P1—S2	112.74 (12)	O1—P1—S1	107.7 (3)
O2—P1—S1	111.69 (13)	O1—P1—S2	112.4 (3)
P1—S1—Zn1	81.48 (5)	O1—P1—O2	100.4 (3)
C31—O4—P2	122.0 (2)	O2—P1—Cd1	122.7 (3)
C1—O1—P1	127.7 (3)	O2—P1—S1	110.2 (3)

C21—O3—P2	121.8 (2)	O2—P1—S2	110.7 (3)
C11—O2—P1	126.1 (2)	P1—S2—Cd1	82.39 (11)
C2—C1—O1	125.4 (4)	S3—P2—S4	115.66 (16)
C6—C1—O1	114.1 (4)	O4—P2—S4	103.2 (3)
C36—C31—O4	118.7 (4)	O4—P2—S3	113.2 (3)
C32—C31—O4	120.1 (3)	O3—P2—S4	112.0 (3)
C16—C11—O2	115.2 (4)	O3—P2—S3	111.2 (3)
C12—C11—O2	123.5 (3)	O3—P2—O4	100.3 (4)
C22—C21—O3	119.6 (4)	P2—S3—Cd1	89.15 (12)
C26—C21—O3	118.6 (4)	C1—O1—P1	124.7 (6)
		C31—O4—P2	121.5 (6)
		C21—O3—P2	127.8 (6)
		C11—O2—P1	120.1 (6)
		C32—C31—O4	118.4 (8)
		C36—C31—O4	120.5 (9)
		O1—C1—C6	116.5 (9)
		C2—C1—O1	124.8 (9)
		C22—C21—O3	123.0 (8)
		C26—C21—O3	115.9 (8)
		C16—C11—O2	118.6 (9)

	C12—C11—O2	120.2 (9)

Symmetry code(s): (i) −*x*+1, *y*, −*z*+3/2; (ii) −*x*+1, −*y*+1, −*z*+1.

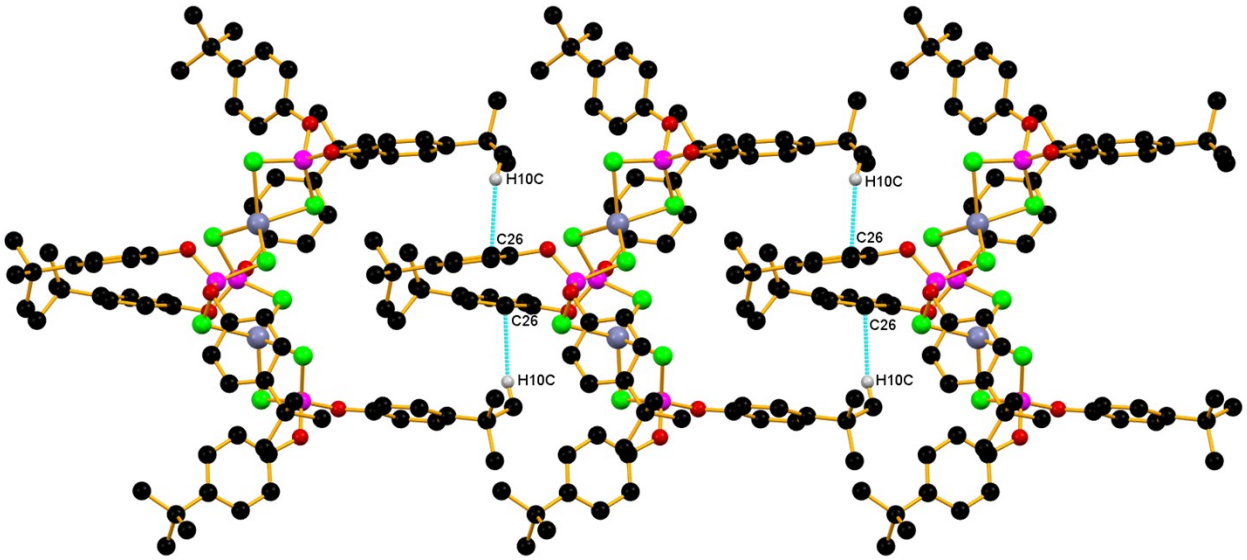

Fig. S1 Supramolecular chain of the complex **1** generated through intermolecular C···H interactions (C6—H10···C26′ = 2.796 Å). Only the relevant hydrogen atoms are shown for clarity. Symmetry transformation (′) = 1 - x, - 1 + y, 1.5 – z.

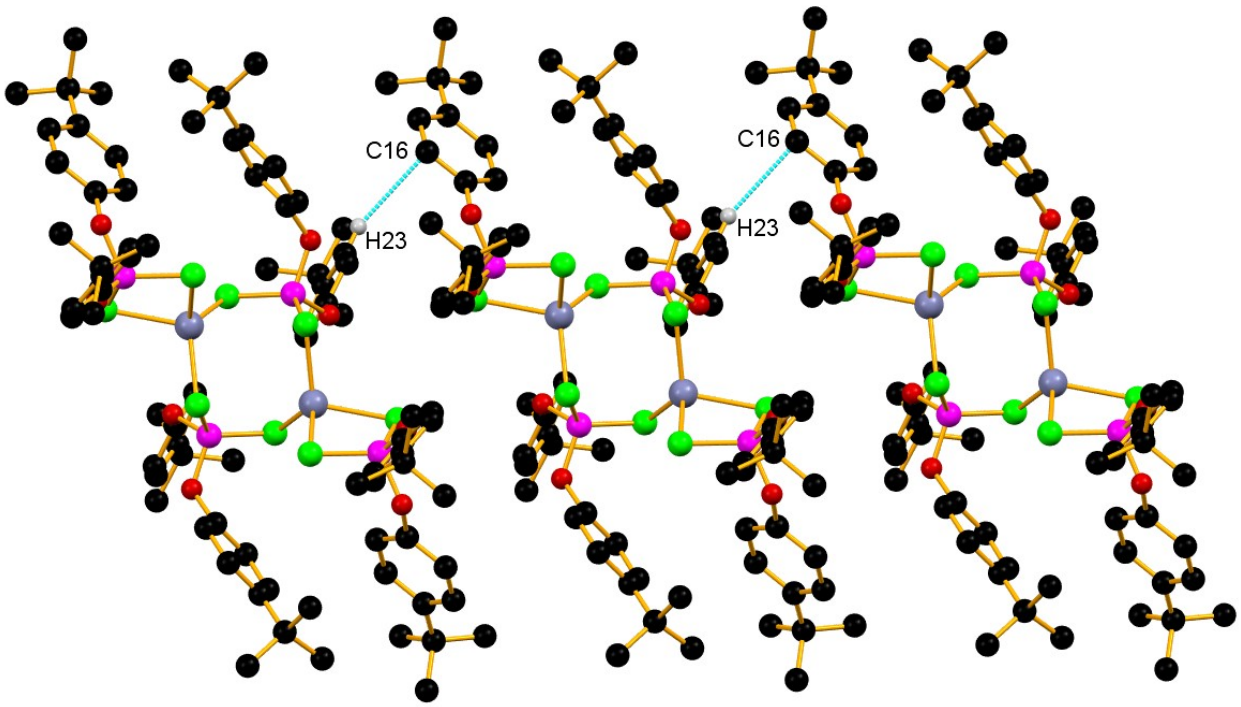

Fig. S2 Supramolecular chain of the complex **1** generated through intermolecular C···H interactions (C23—H23···C16′ = 2.885 Å). Only the relevant hydrogen atoms are shown for clarity. Symmetry transformation (′) = 1/2+x, -1/2+y, +z.

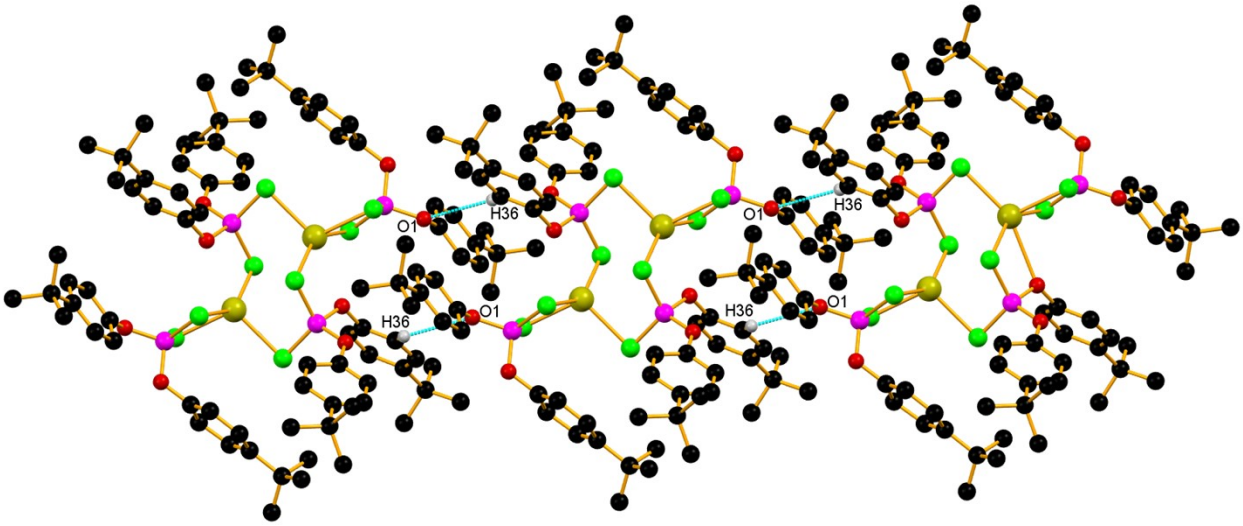

Fig. S3 Supramolecular chain of complex **2** generated through CH···O interactions (C36—H36···O1′ = 2.720 Å). Only the relevant hydrogen atoms are shown for clarity. Symmetry transformation (′) = x, -1 + y, z.

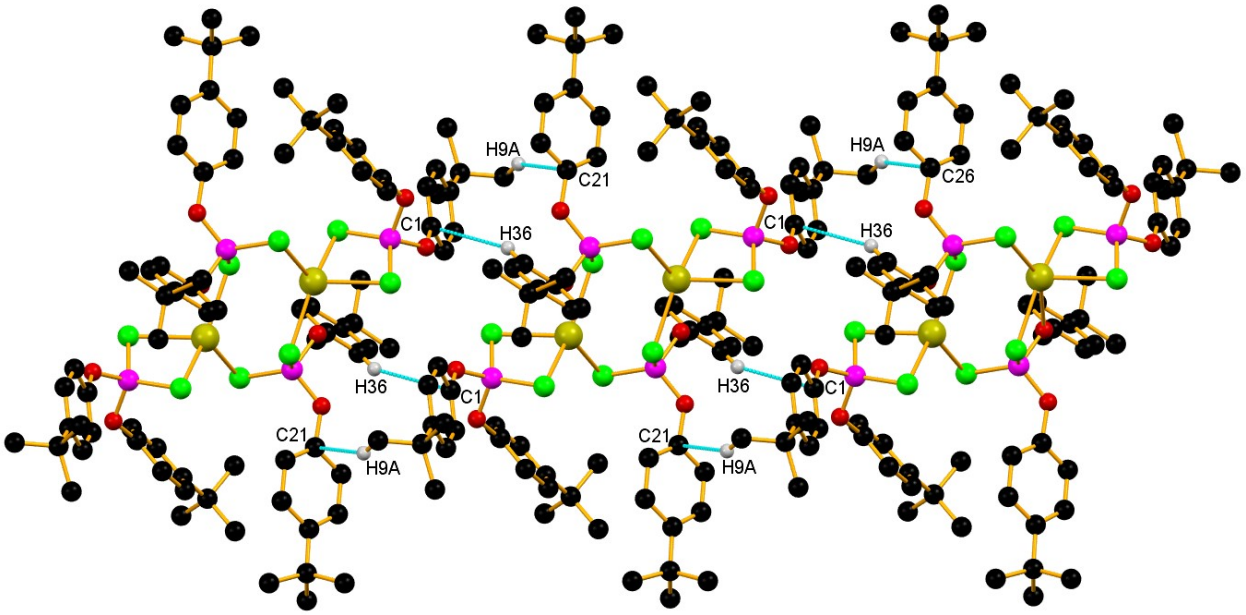

Fig. S4 Supramolecular chain of the complex **2** generated through intermolecular C···H interactions (C36—H36···C1′ = 2.847 Å and C9—H9A··· C21′ = 2.889 Å). Only the relevant hydrogen atoms are shown for clarity. Symmetry transformation (′) = x, -1 + y, z.

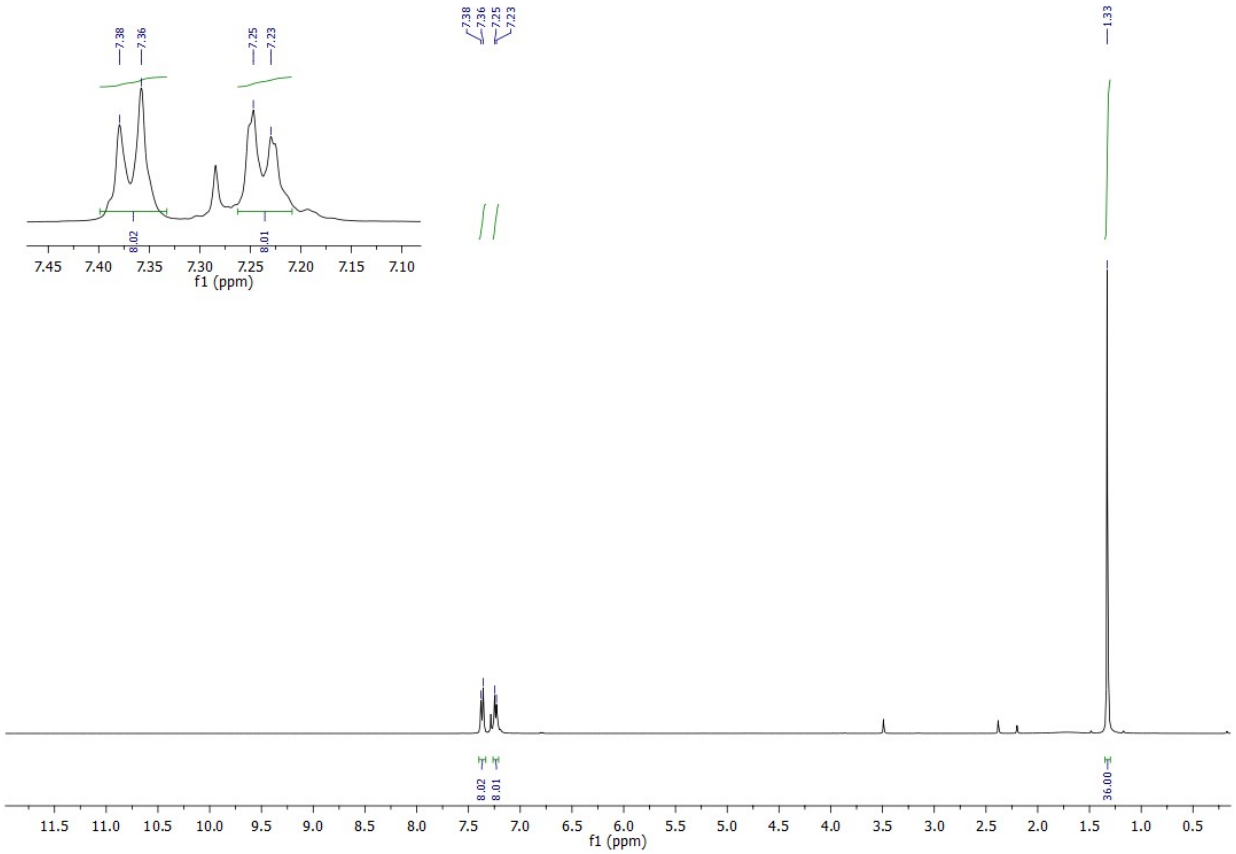

Fig. S5 ^{1}H NMR spectra of complex **1** ($CDCl_3$)

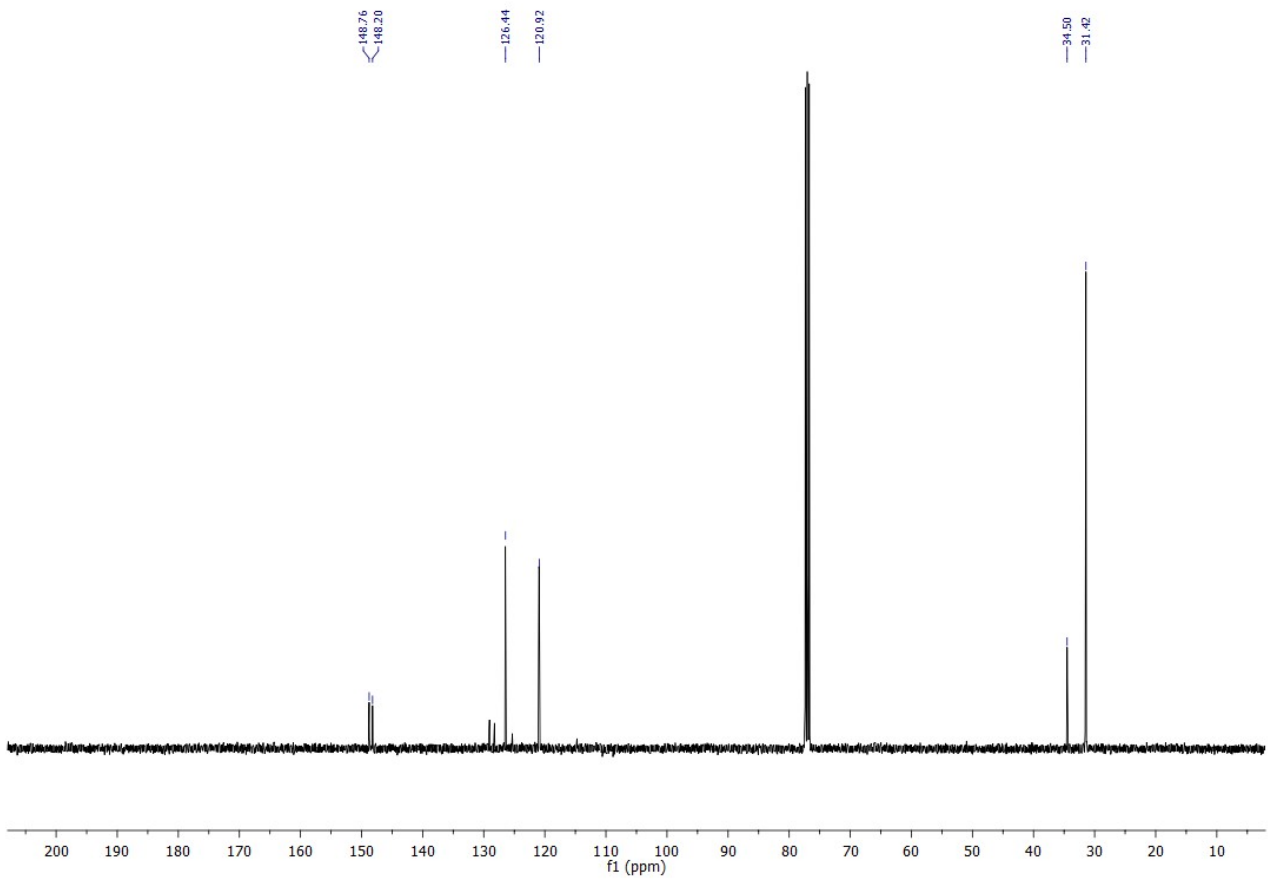

Fig. S6 ^{13}C NMR spectra of complex **1** ($CDCl_3$)

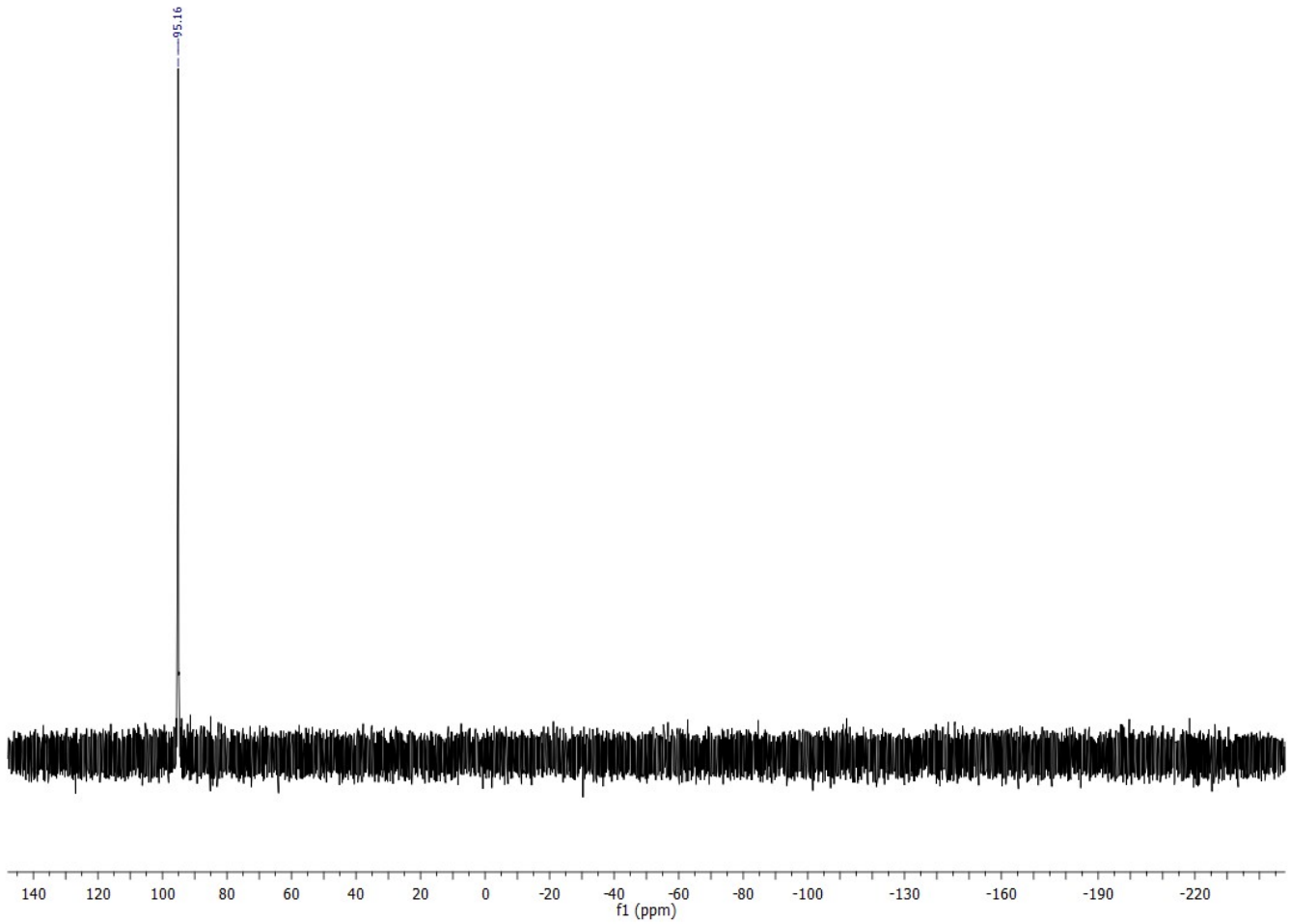

Fig. S7 ^{31}P NMR spectra of complex **1** ($CDCl_3$)

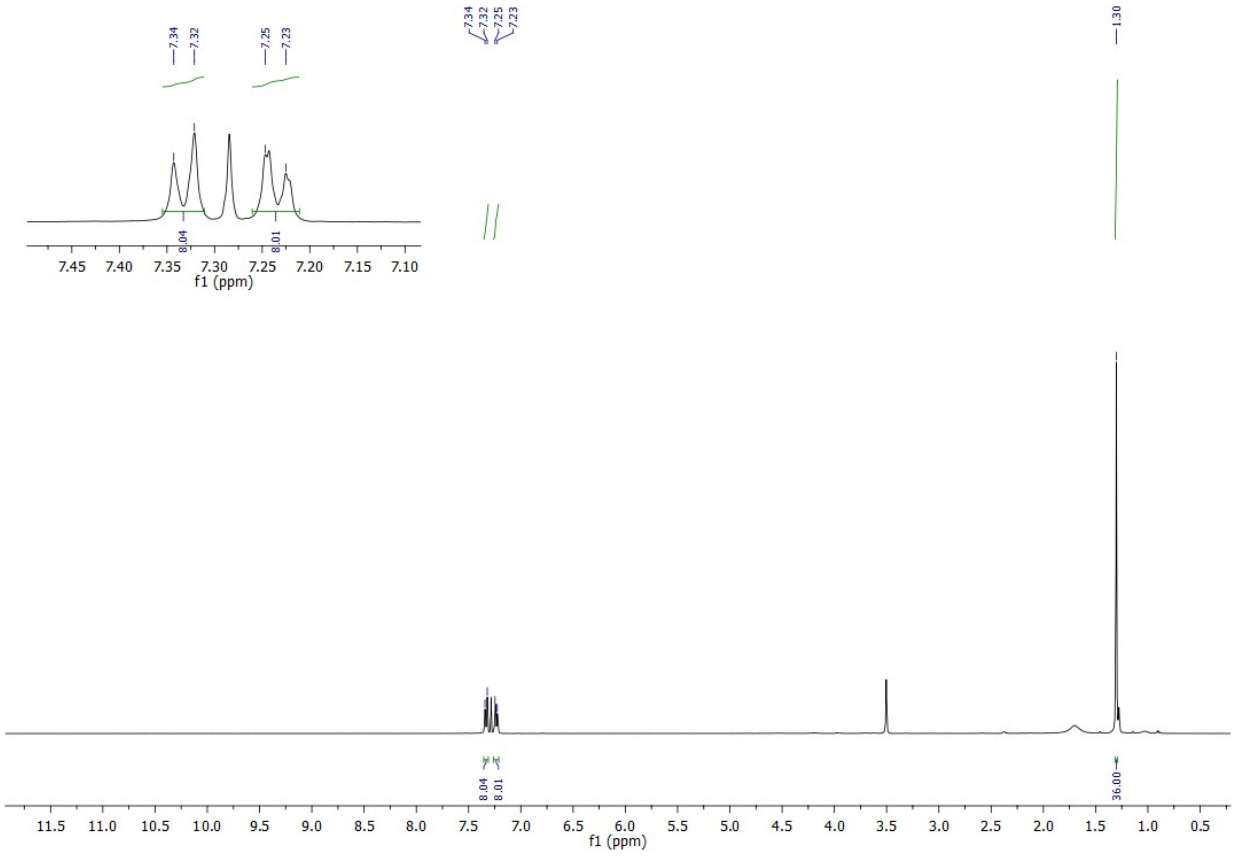

Fig. S8 ^{1}H NMR spectra of complex **2** ($CDCl_3$)

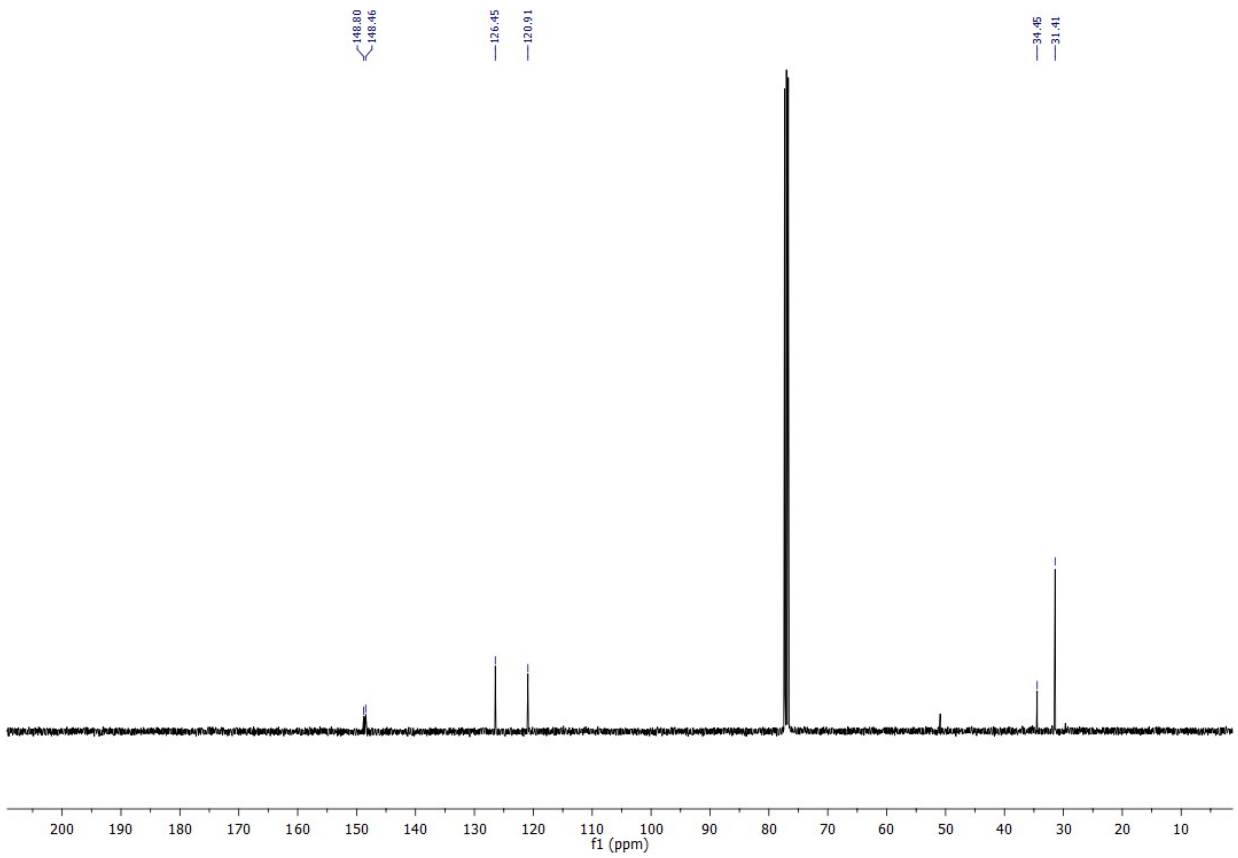

Fig. S9 ^{13}C NMR spectra of complex **2** ($CDCl_3$)

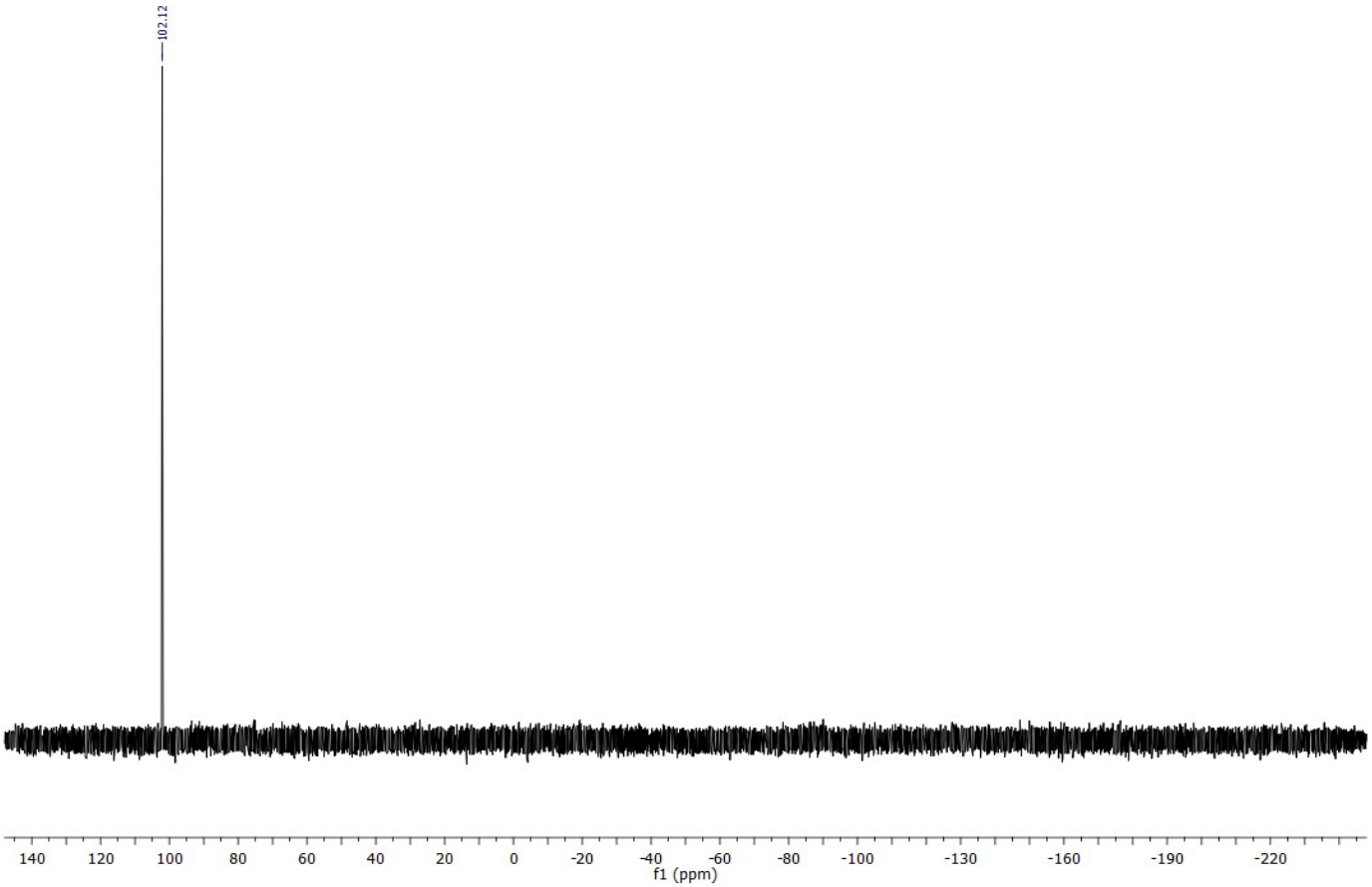

Fig. S10 ^{31}P NMR spectra of complex **2** ($CDCl_3$)

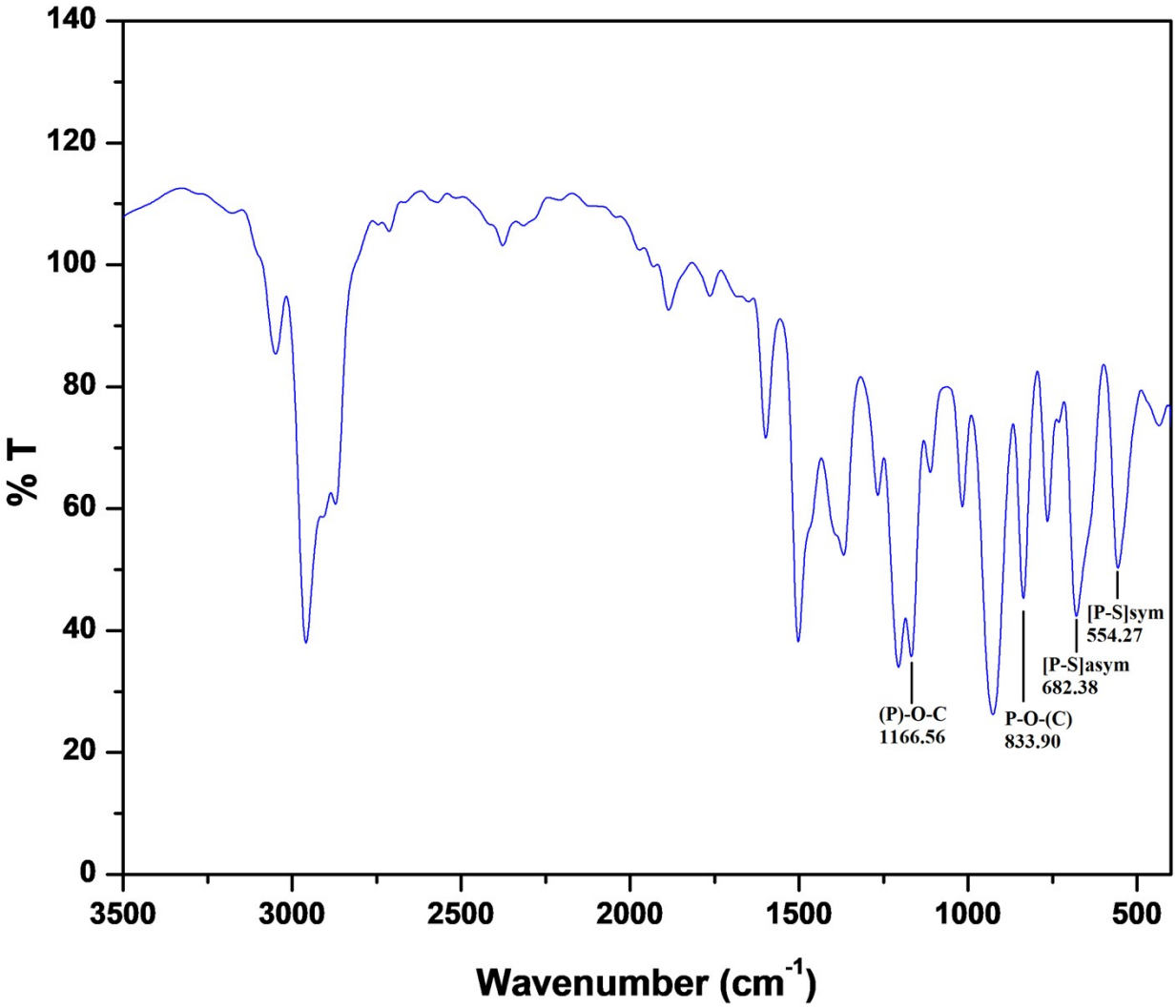

Fig. S11 FTIR spectra of complex **1**

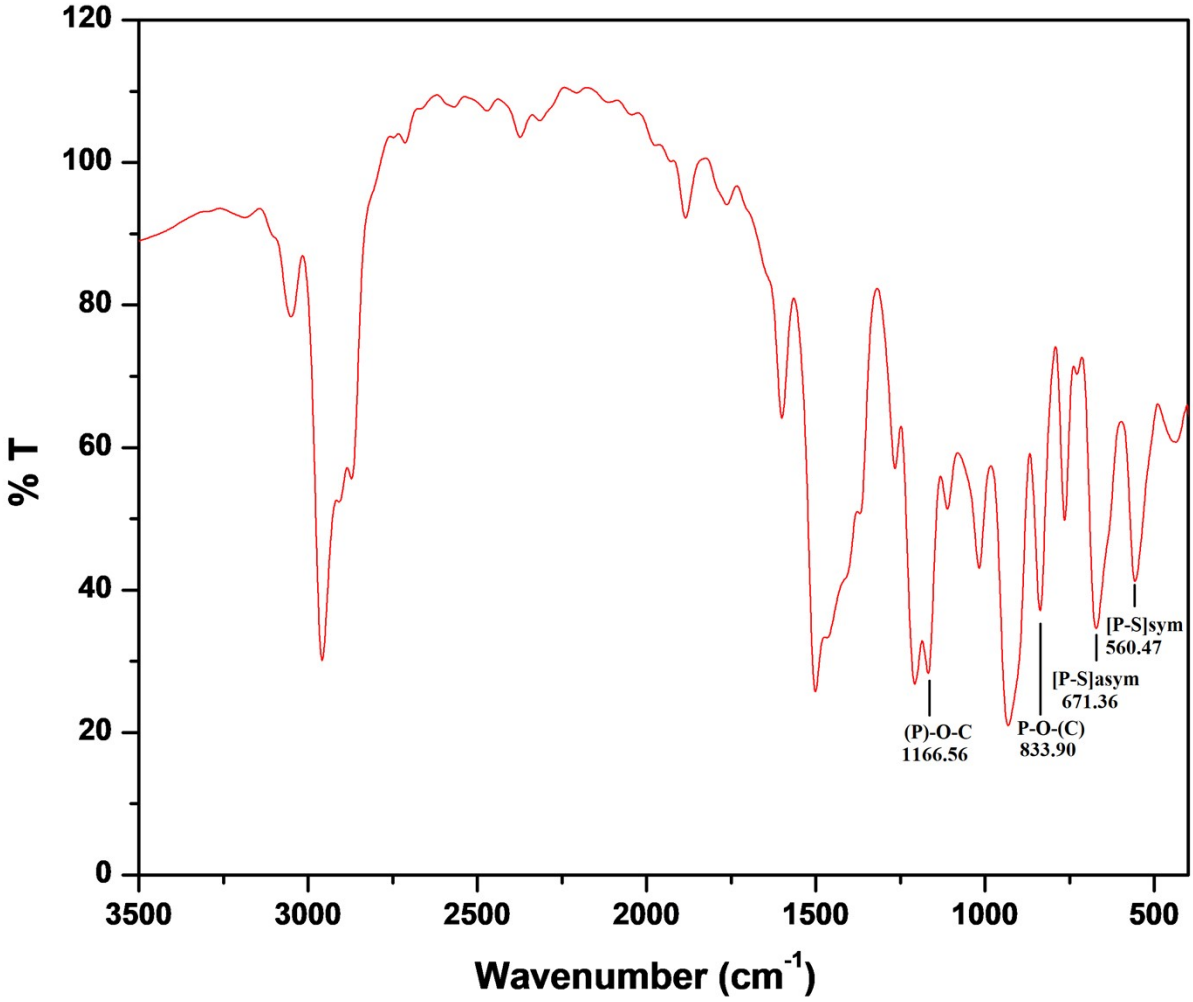

Fig. S12 FTIR spectra of complex **2**

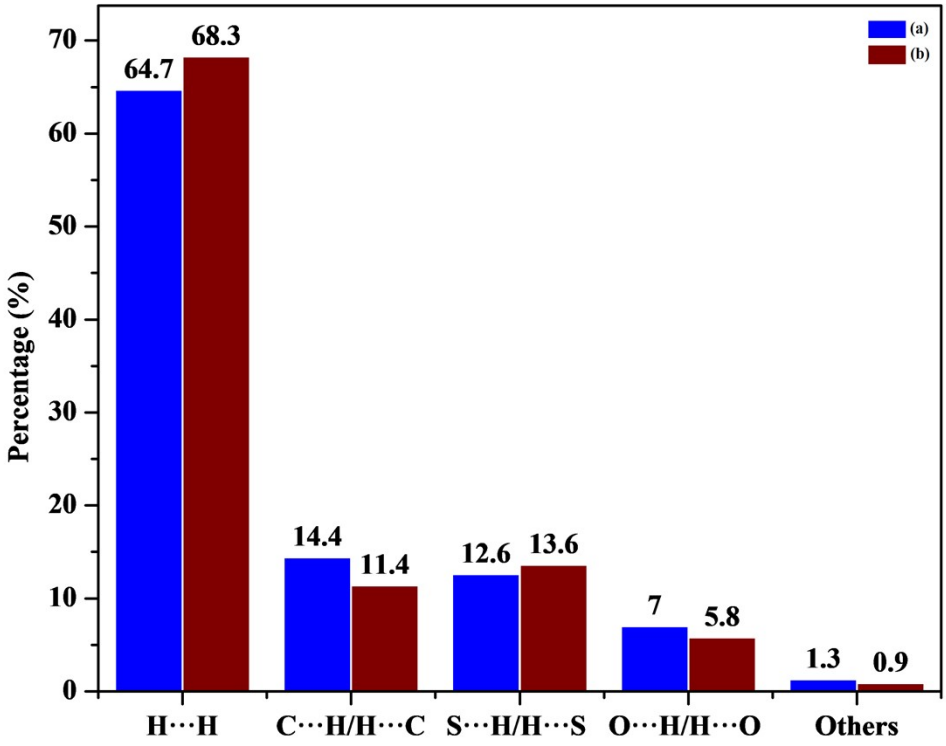

Fig. S13 Relative contributions of various intermolecular contacts to the Hirshfeld surface area of complexes (a) **1** and (b) **2**.