Elementary Supporting Information

An insight into triel bonds in *O,O'*-diarylphosphorodithioates of thallium(I): Experimental and theoretical investigations

Tahira Firdoos,[a] Pretam Kumar,[a] Anu Radha,[a] Rosa M. Gomila,[b] Antonio Frontera,[b] Puneet Sood[c] and Sushil K. Pandey*[a]

[a]*Post Graduate Department of Chemistry, University of Jammu, Baba Saheb Ambedkar Road, Jammu Tawi-180006, J&K, India*

[b]*Departament de Química, Universitat de les Illes Balears, Crta de Valldemossa km 7.5, 07122 Palma de Mallorca (Baleares), Spain*

[c]*Advanced Materials Research Center, Block-A2 Building, Kamand Campus, Indian Institute of Technology, Mandi, Himachal Pradesh-175005, India.*

**Email: kpsushil@rediffmail.com*

Table S1 Crystallographic parameter for compounds **1** and **2**

Compound	**1**	**2**
CCDC	2109341	2109342
Chemical formula	$C_{16}H_{18}O_2PS_2Tl$	$C_{18}H_{22}O_2PS_2Tl$
M_r	541.81	569.82
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	10.9662 (3)	8.4373 (8)
b (Å)	11.3253 (4)	9.6672 (9)
c (Å)	14.7907 (4)	12.6725 (19)

α (°)	90	107.092 (11)
β (°)	100.286 (3)	95.785 (10)
γ (°)	90	90.443 (8)
V (Å^3)	1807.42 (10)	982.2 (2)
Z	4	2
μ (mm^{-1})	9.26	8.52
Crystal size (mm)	0.26 × 0.2 × 0.14	0.18 × 0.08 × 0.06
Data collection		
Diffractometer	SuperNova, Dual, Cu at home/near, Eos	SuperNova, Dual, Cu at home/near, Eos
T_{min}, T_{max}	0.278, 0.578	0.496, 1.000
No. of measured, independent and observed reflections	5950, 3894, 3154 [$I \geq 2u(I)$]	5647, 4026, 3316 [$I > 2\sigma(I)$]
R_{int}	0.048	0.108
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.668	0.668
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.045, 0.123, 1.00	0.089, 0.222, 1.05
No. of reflections	3894	4026
No. of parameters	201	221
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.64, −1.28	4.81, −3.11

Table S2 Selected bond lengths of complexes **1** and **2** (Å)

Complex 1		**Complex 2**	
Tl1—S21	3.0648 (18)	Tl2—S2	2.986 (4)
Tl1—S22	3.169 (2)	Tl2—S4^{i}	3.110 (4)
S21—P9	1.971 (3)	S2—P5	1.957 (5)
S22—P9	1.970 (3)	S4—Tl2^{i}	3.110 (4)
P9—O8	1.615 (5)	S4—P5	1.973 (5)
P9—O10	1.605 (5)	P5—O3	1.634 (11)
O8—C2	1.384 (8)	P5—O10	1.621 (11)
O10—C11	1.405 (9)	O3—C24	1.388 (17)
		O10—C33	1.377 (17)

Symmetry code(s): (i) −*x*, −*y*+1, −*z*+1.

Table S3 Selected bond angles of complexes **1** and **2** (º)

Complex 1		**Complex 2**	
S22—Tl1—S21	63.78 (5)	S2—Tl2—S4^{i}	87.65 (11)
P9—S21—Tl1	86.58 (8)	P5—S2—Tl2	88.57 (18)
P9—S22—Tl1	83.71 (8)	P5—S4—Tl2^{i}	109.84 (19)
S22—P9—S21	113.43 (12)	S2—P5—S4	116.4 (2)
O8—P9—S21	111.6 (2)	O3—P5—S2	112.5 (5)

O8—P9—S22	111.8 (2)	O3—P5—S4	110.9 (4)
O10—P9—S21	113.6 (2)	O10—P5—S2	111.2 (4)
O10—P9—S22	111.6 (2)	O10—P5—S4	111.3 (5)
O10—P9—O8	93.2 (3)	O10—P5—O3	92.0 (6)
C2—O8—P9	120.1 (4)	C24—O3—P5	122.1 (9)
C11—O10—P9	120.5 (4)	C33—O10—P5	125.6 (9)
C3—C2—O8	119.8 (6)	C1AA—C24—O3	117.9 (13)
C7—C2—O8	119.3 (7)	C20—C24—O3	120.1 (13)
C12—C11—O10	120.8 (7)	O10—C33—C26	123.2 (13)
C16—C11—O10	118.2 (7)	O10—C33—C30	116.7 (14)

Symmetry code(s): (i) −*x*, −*y*+1, −*z*+1.

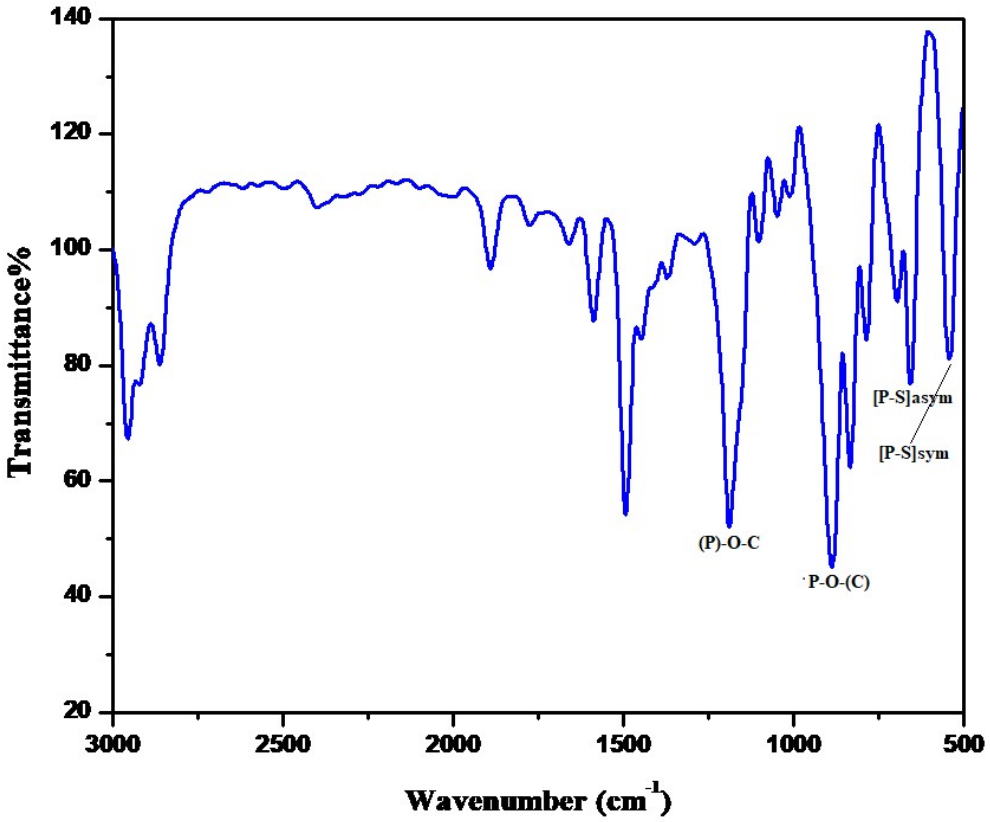

Fig. S1 FTIR spectra of Compound **1**

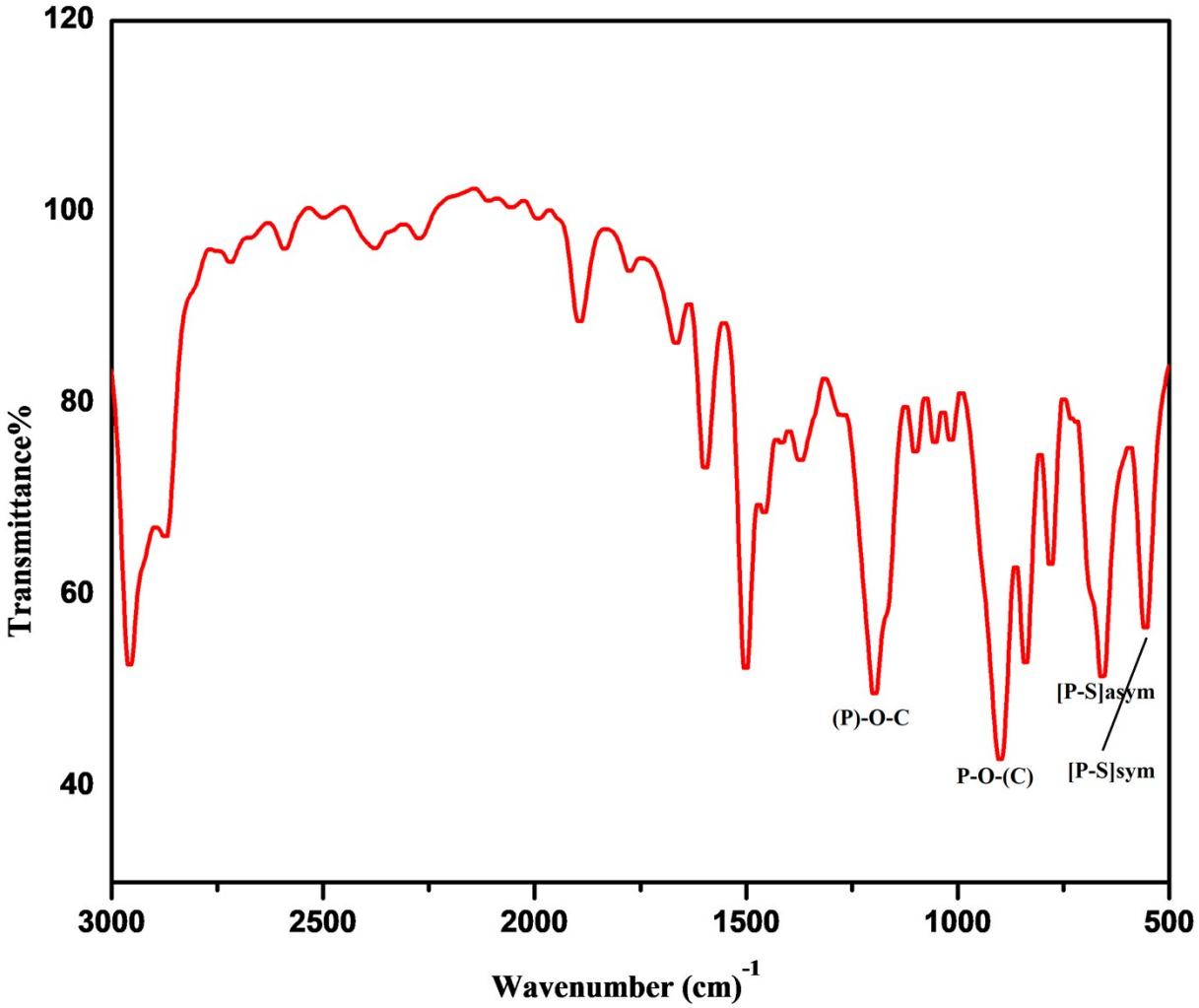

Fig. S2 FTIR spectra of Compound **2**

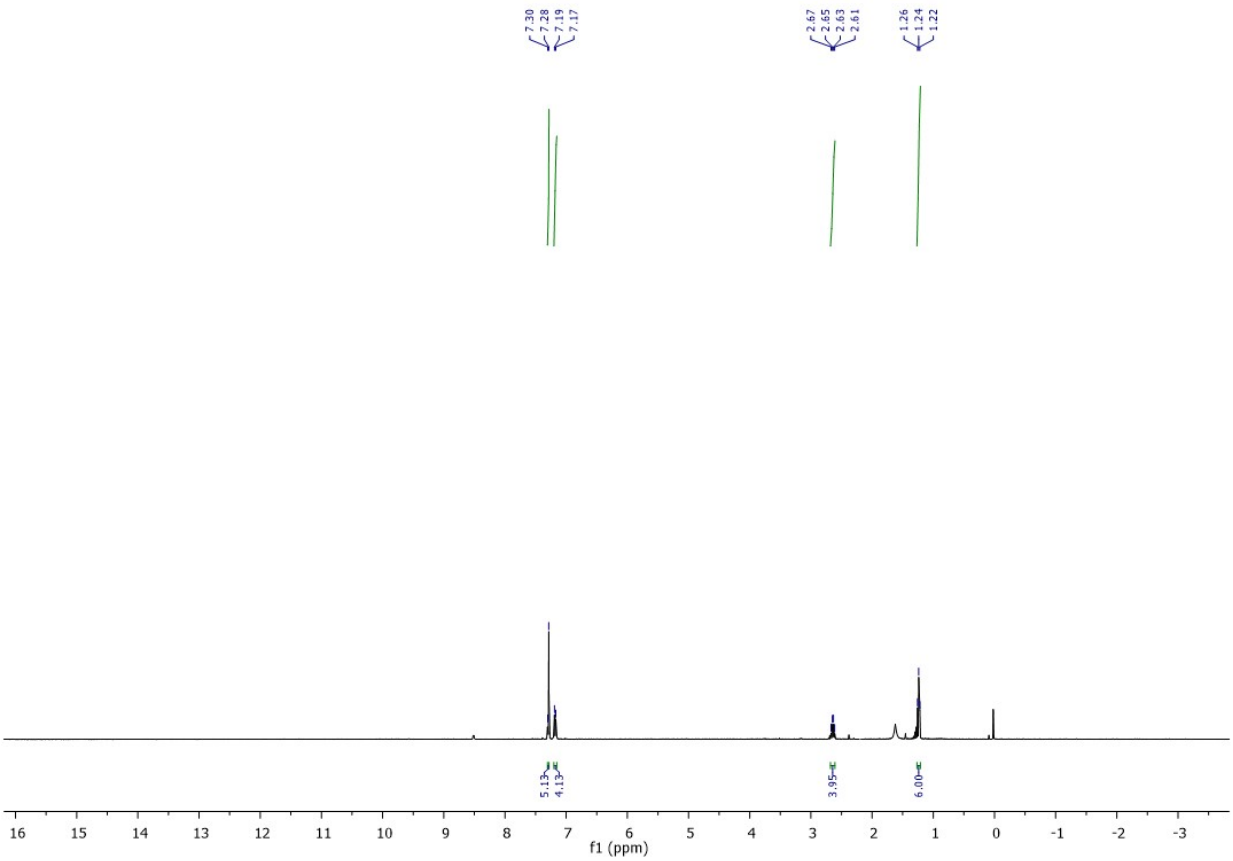

Fig. S3 ^{1}H NMR spectra of Compound **1** ($CDCl_3$)

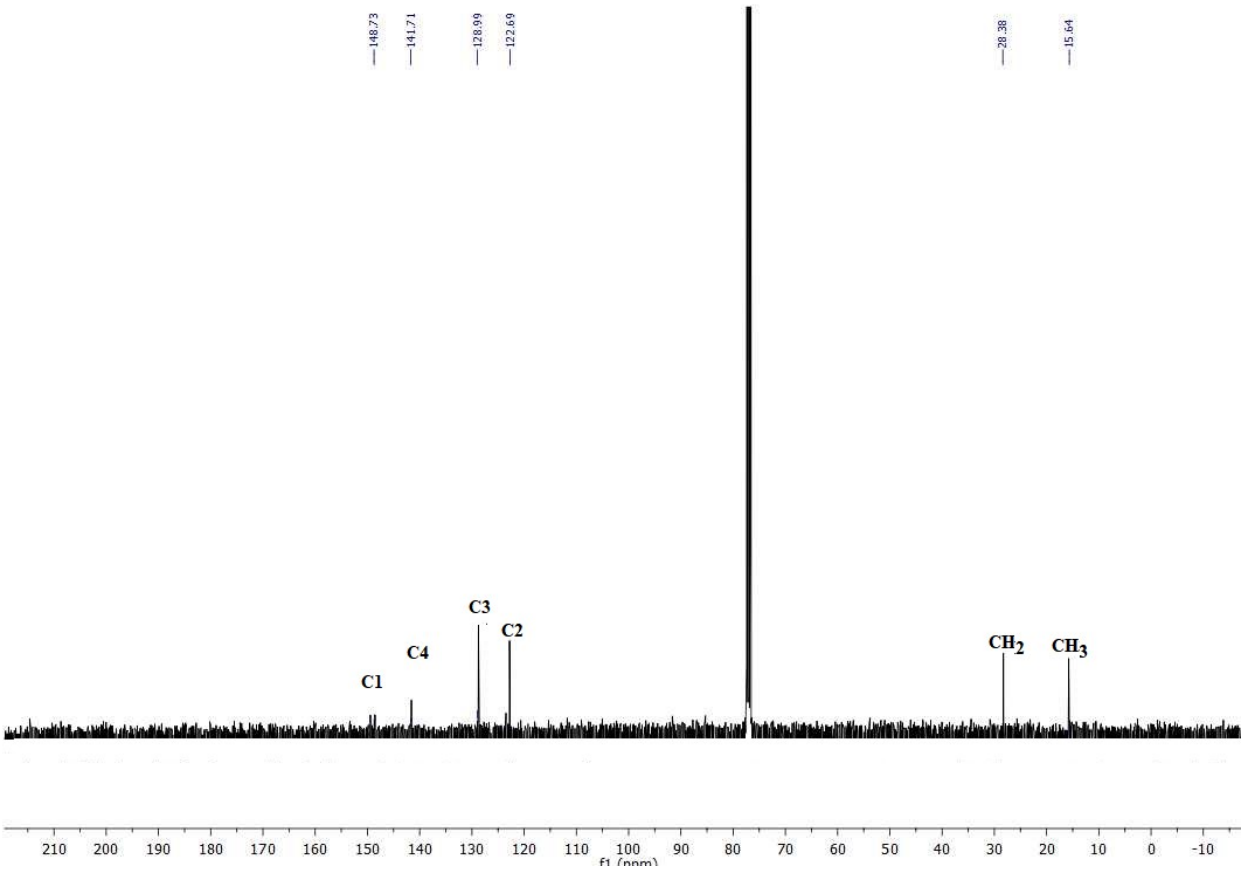

Fig. S4 ^{13}C NMR spectra of Compound **1** ($CDCl_3$)

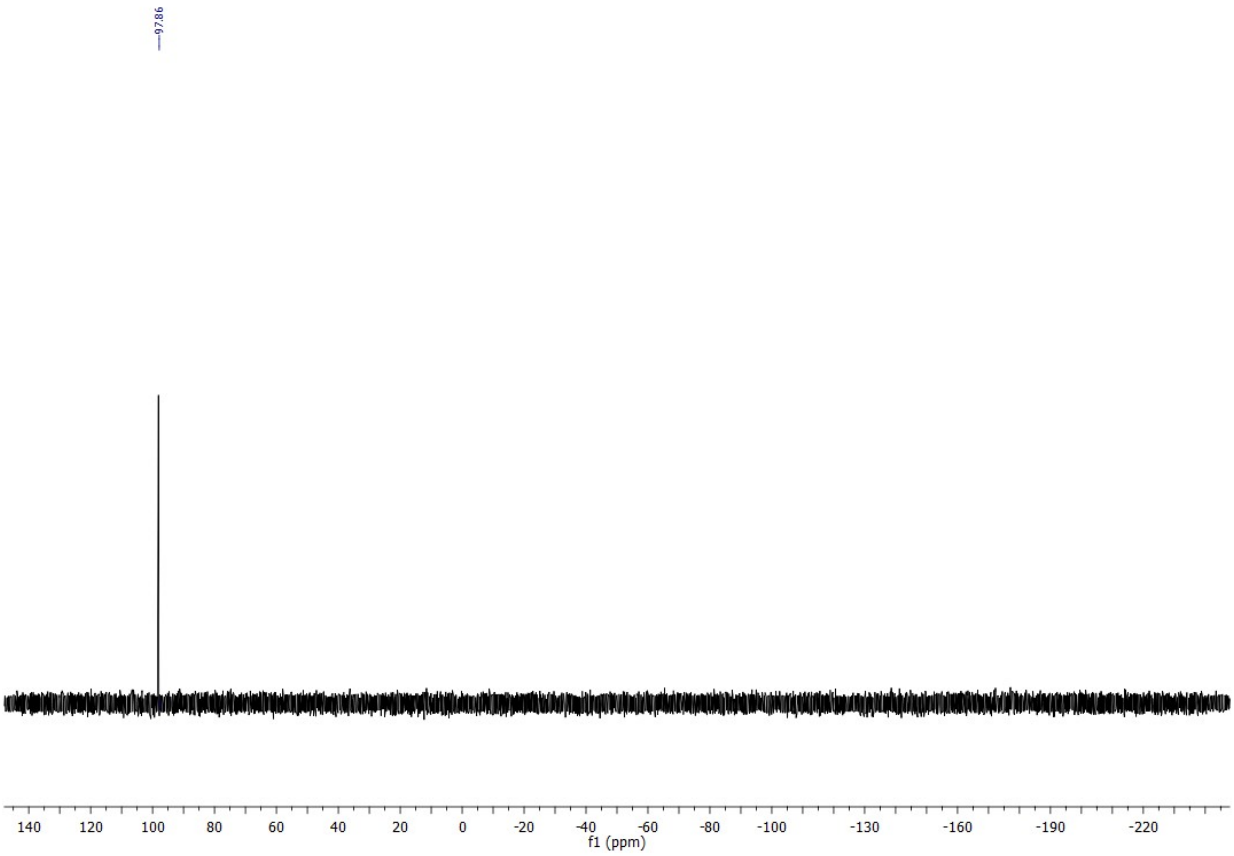

Fig. S5 ^{31}P NMR spectra of Compound **1** ($CDCl_3$)

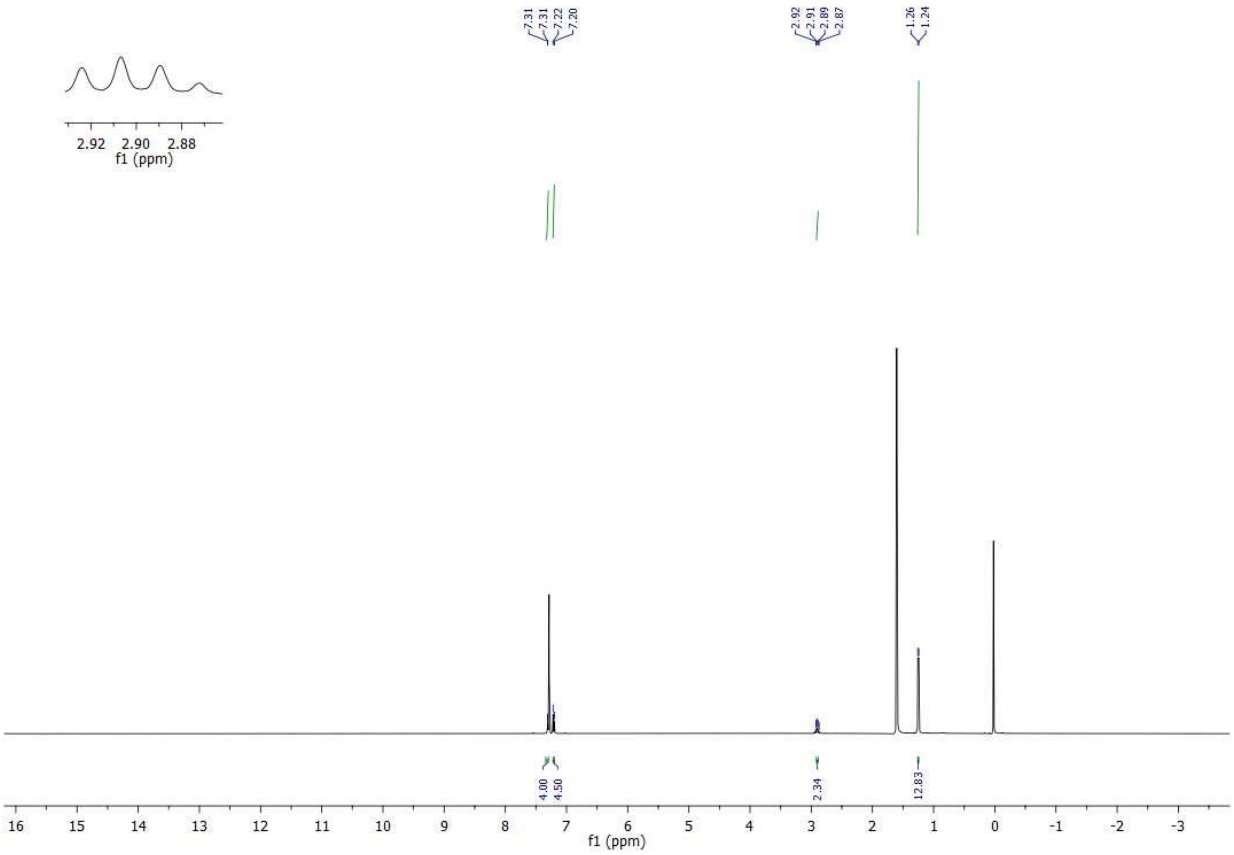

Fig. S6 ^{1}H NMR spectra of Compound **2** ($CDCl_3$)

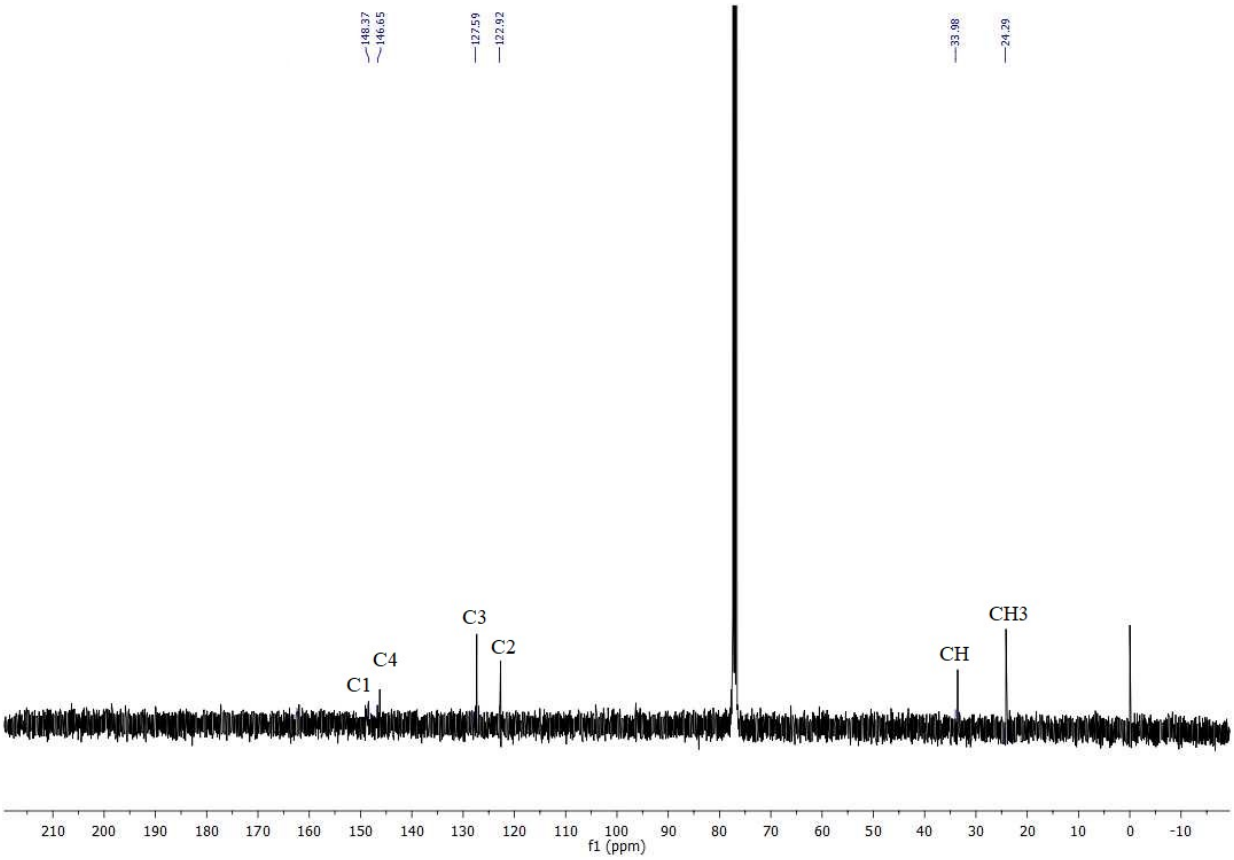

Fig. S7 ^{13}C NMR spectra of Compound **1** ($CDCl_3$)

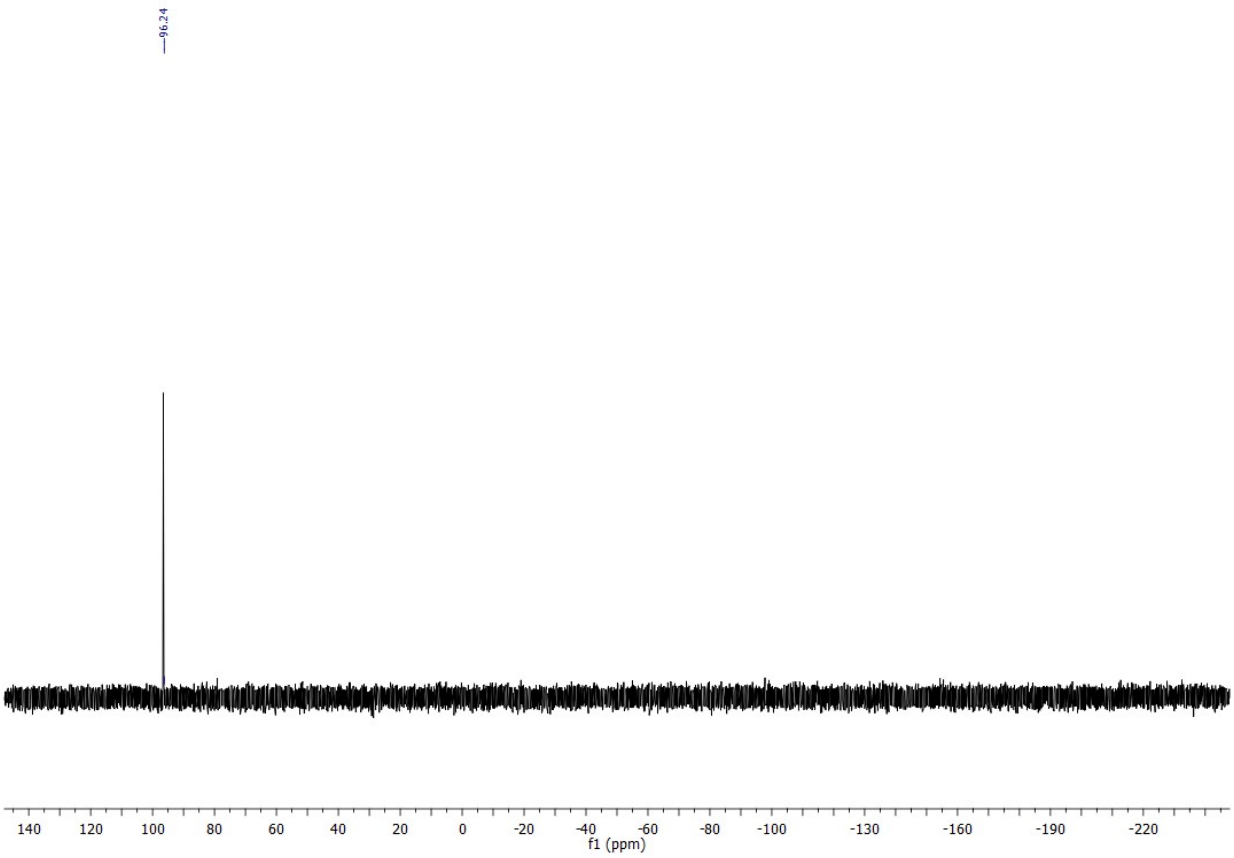

Fig. S8 ^{31}P NMR spectra of Compound **2** ($CDCl_3$)

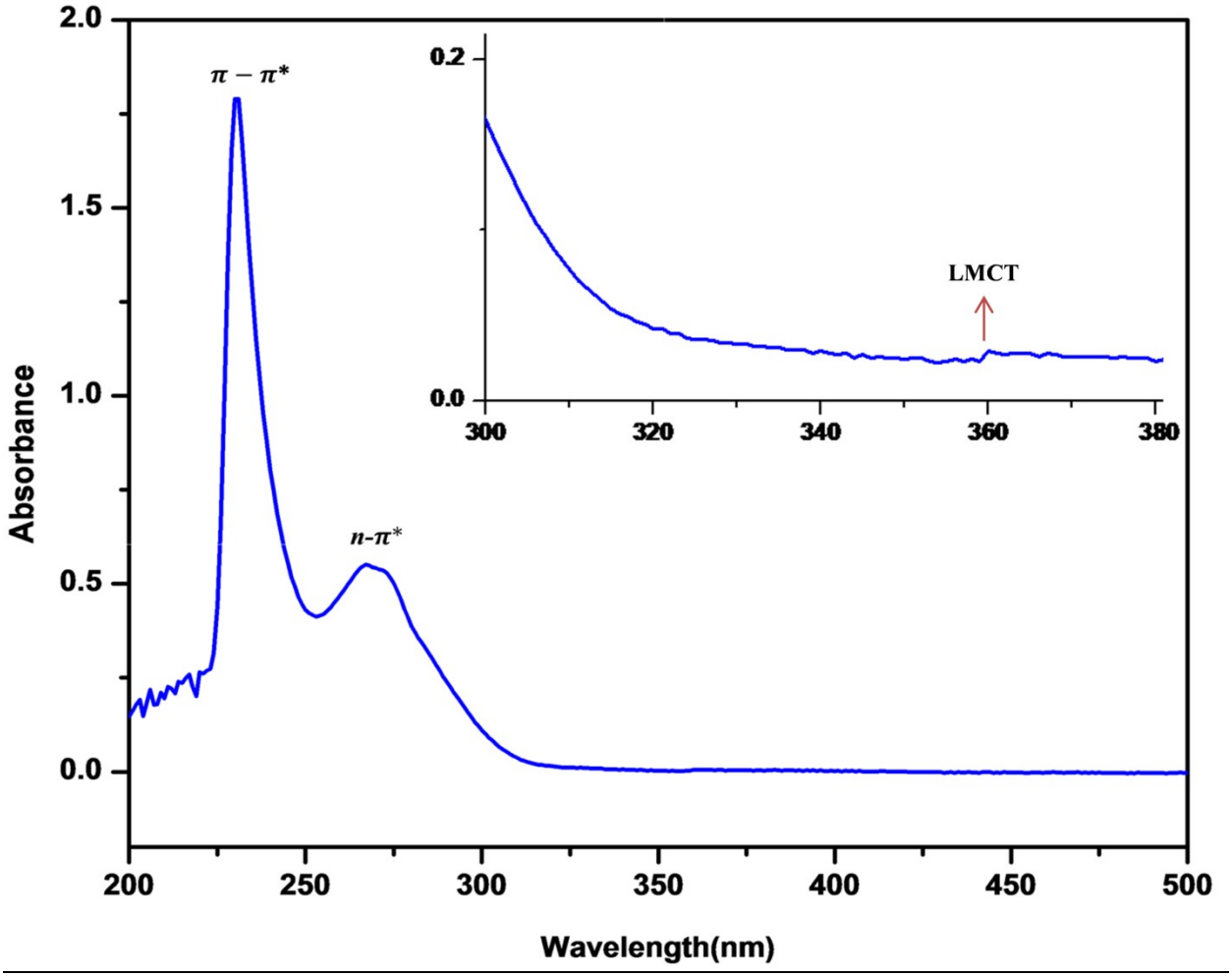

Fig. S9 UV-Vis spectra of Compound **1**

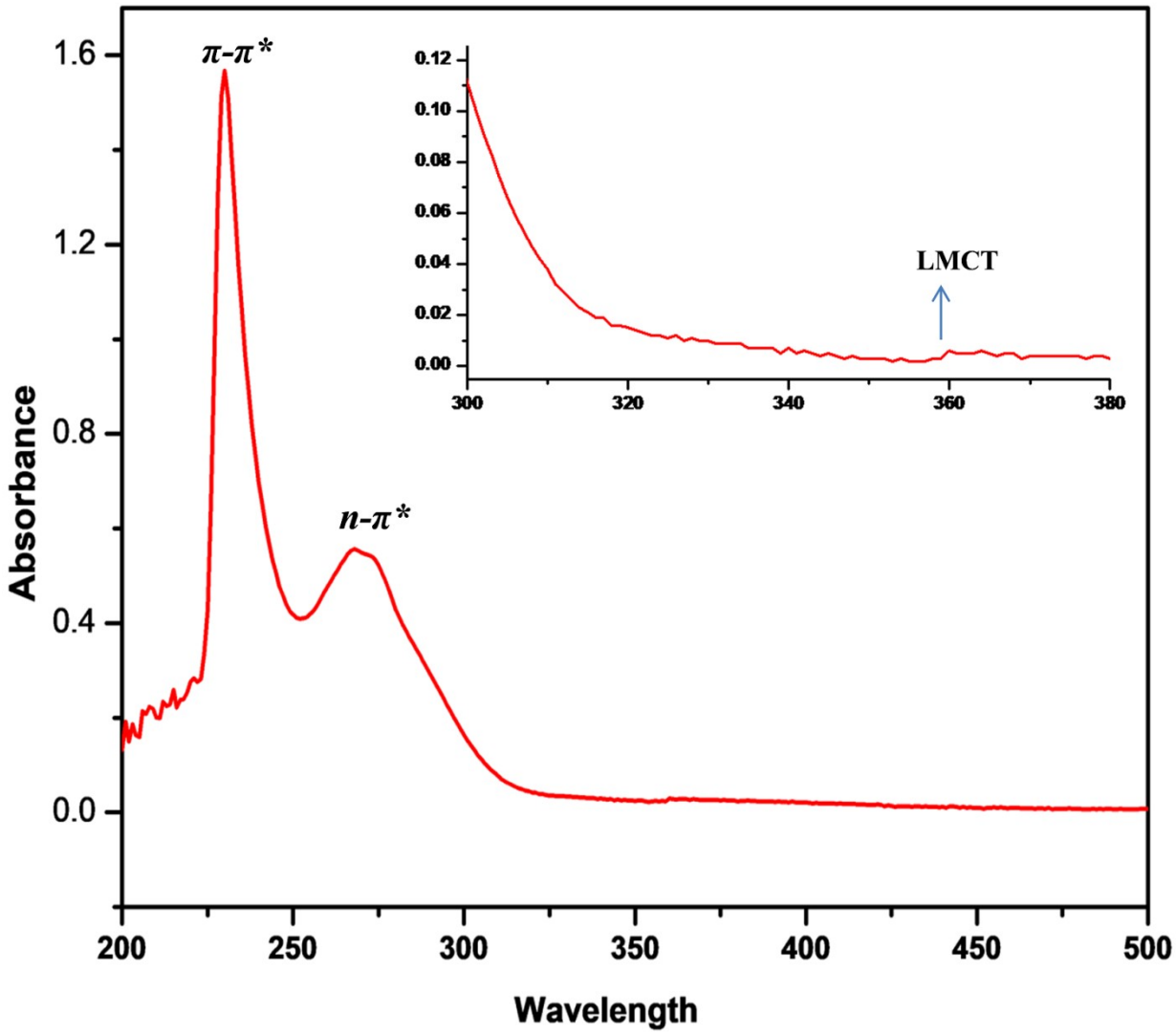

Fig. S10 UV-Vis spectra of Compound **2**

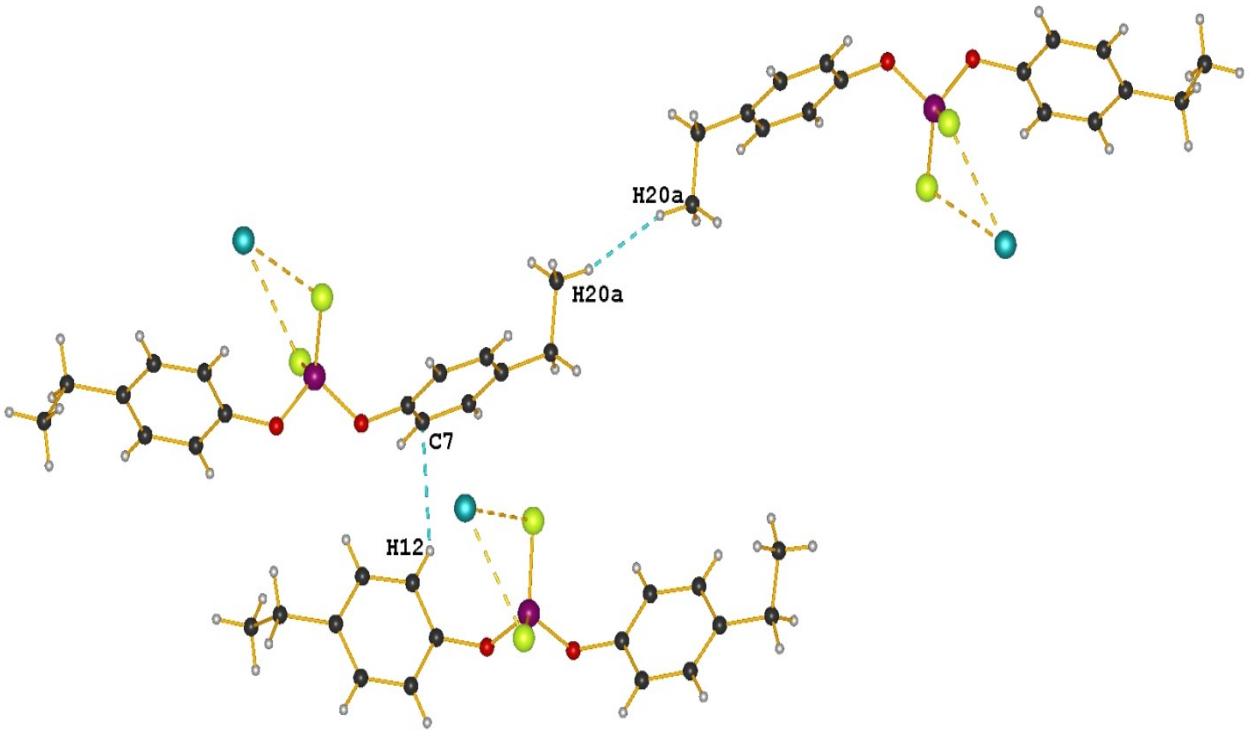

Fig. S11 Supramolecular motif of compound **1** generated through C···H and H···H interactions.

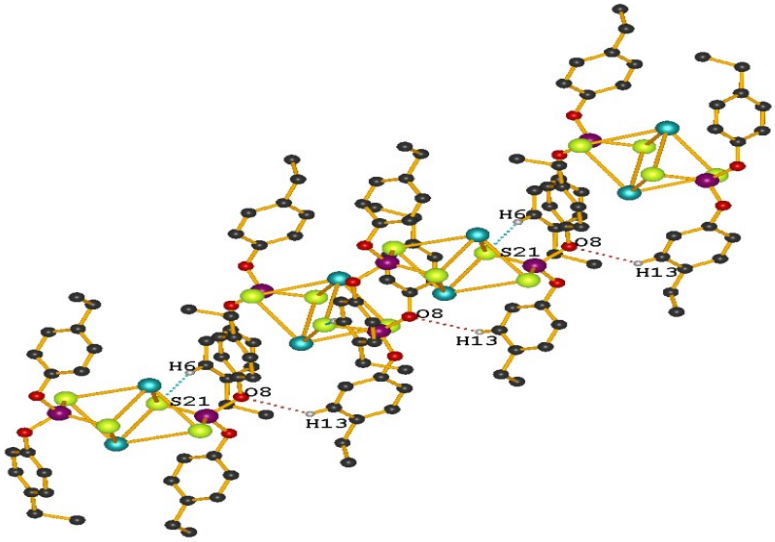

Fig. S12 Polymeric chain of compound **1** generated through intermolecular O···H and S···H interactions. Only the relevant hydrogen atoms are shown for clarity. Symmetry transformation

for H···O = x, 1.5 − y, − 1/2 + z where H13···O8 = 2.57 Å and symmetry transformation for H···S = 1 − x, − 1/2 +y, 1/2 − z where H6···S21 = 2.98 Å.

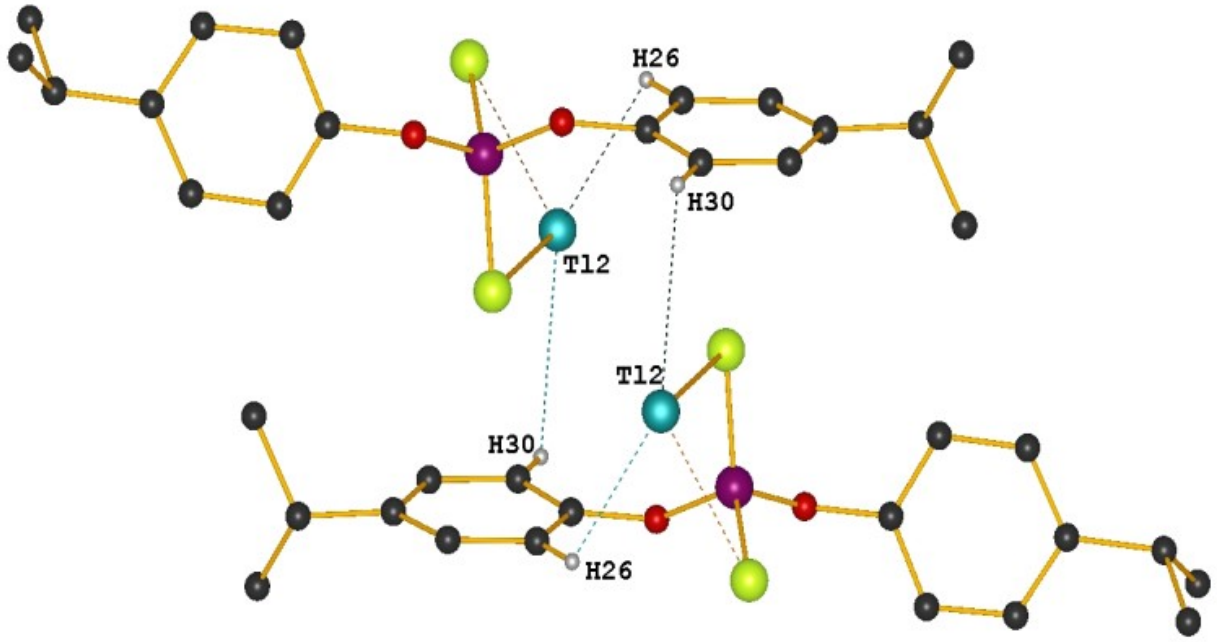

Fig. S13 Supramolecular dimer of compound **2** generated through anagostic C–H···Tl anagostic interactions. Only the relevant Hydrogen atoms are shown for clarity. Symmetry transformation = x, y, z where C–H26···Tl2 = 3.30 Å.

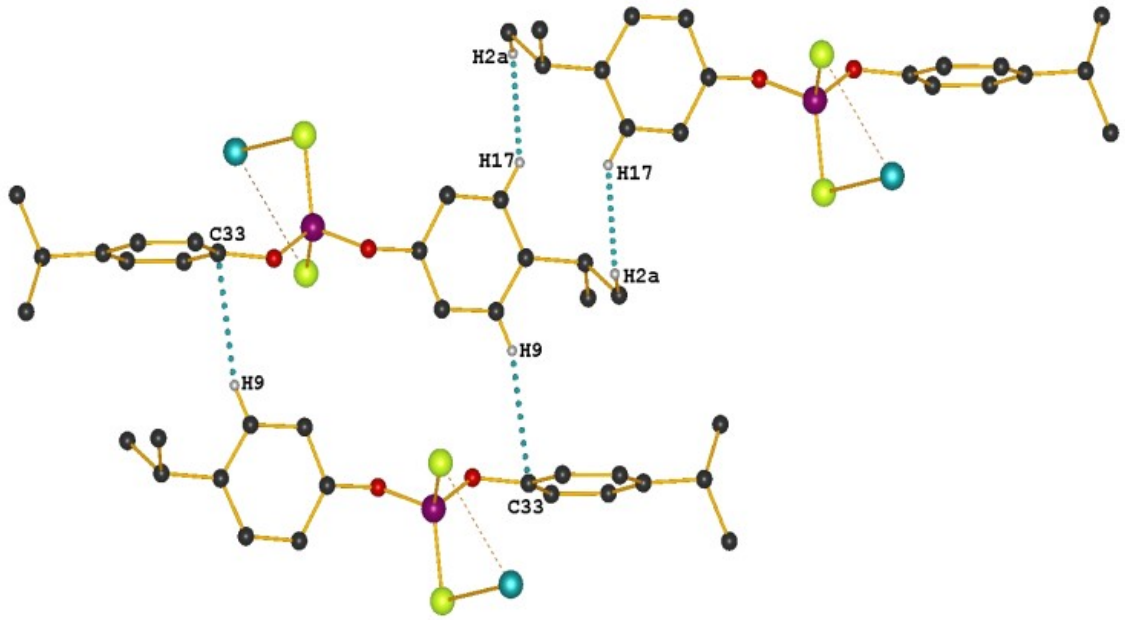

Fig. S14 Supramolecular dimer of compound **2** generated via C···H and H···H interactions. Symmetry transformation = 1 − x, 1 − y, 1 − z with H9···C33 = 2.82 Å.

Table S4 QTAIM parameters (a.u.) measured at the bond critical points (CP) labelled in Figs. 12 and 13 for the Tl···S contacts in compounds **1** and **2**.

BCP	ρ_r	$\nabla^2\rho_r$	V_r	G_r	H_r
Compound **1**					
a	0.0262	0.0555	−0.0159	0.0149	–0.0010
b	0.0216	0.0468	−0.0121	0.0119	–0.0002
c	0.0144	0.0322	−0.0068	0.0074	0.0062
d	0.0207	0.0444	−0.0112	0.0112	0.0000
Compound **2**					
a	0.0303	0.0620	−0.0195	0.0175	–0.0020
b	0.0208	0.0450	−0.0114	0.0113	–0.0001
c	0.0231	0.0496	−0.0131	0.0127	–0.0004
d	0.0110	0.0239	−0.0045	0.0052	0.0007