SUPPLEMENTARY DATA

Exploration of fluorescent organotin compounds of α-amino acid Schiff bases for the recognition of organophosphorous chemical warfare agents: Quantification of diethylchlorophosphate

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Characterization

Compound 1

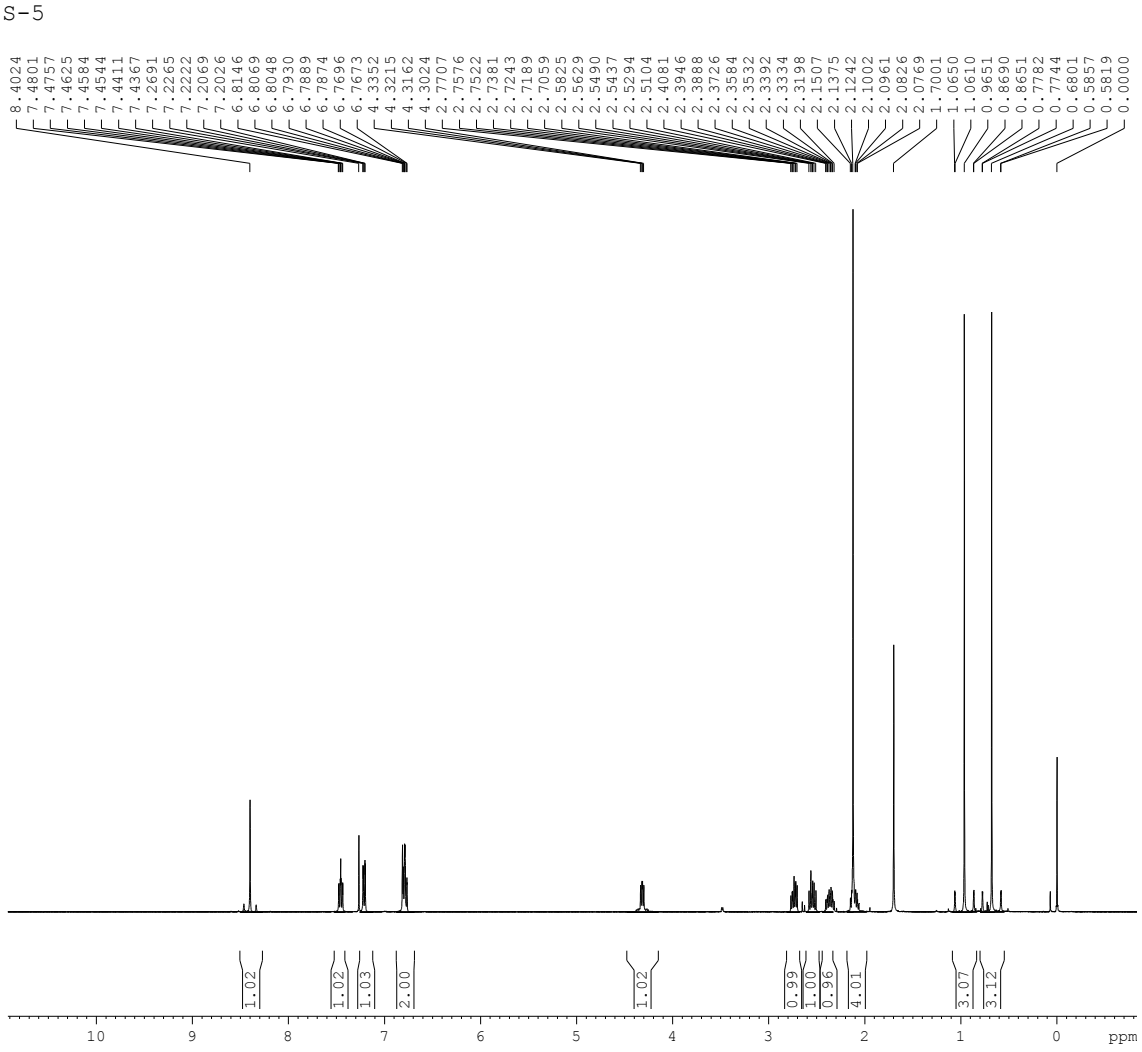


Fig. S1(a) [1]HNMR spectrum of compound **1**.

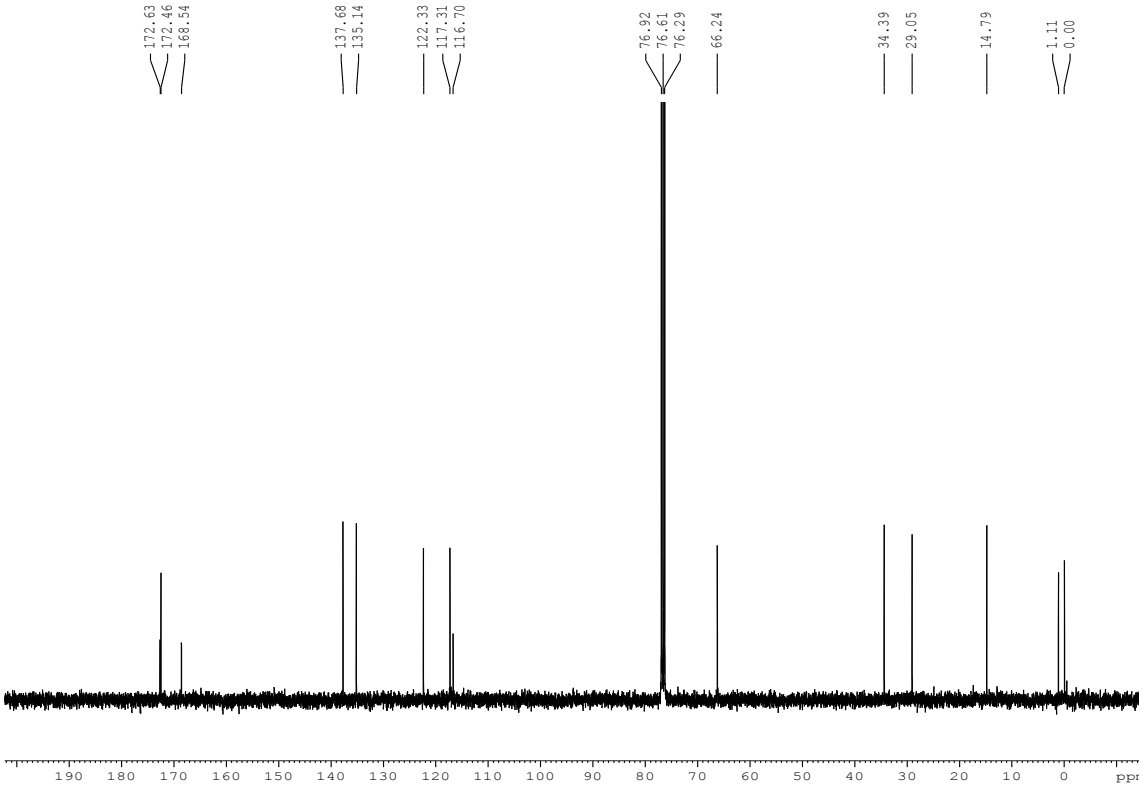


Fig S1(b) ^{13}C NMR spectrum of compound **1**.

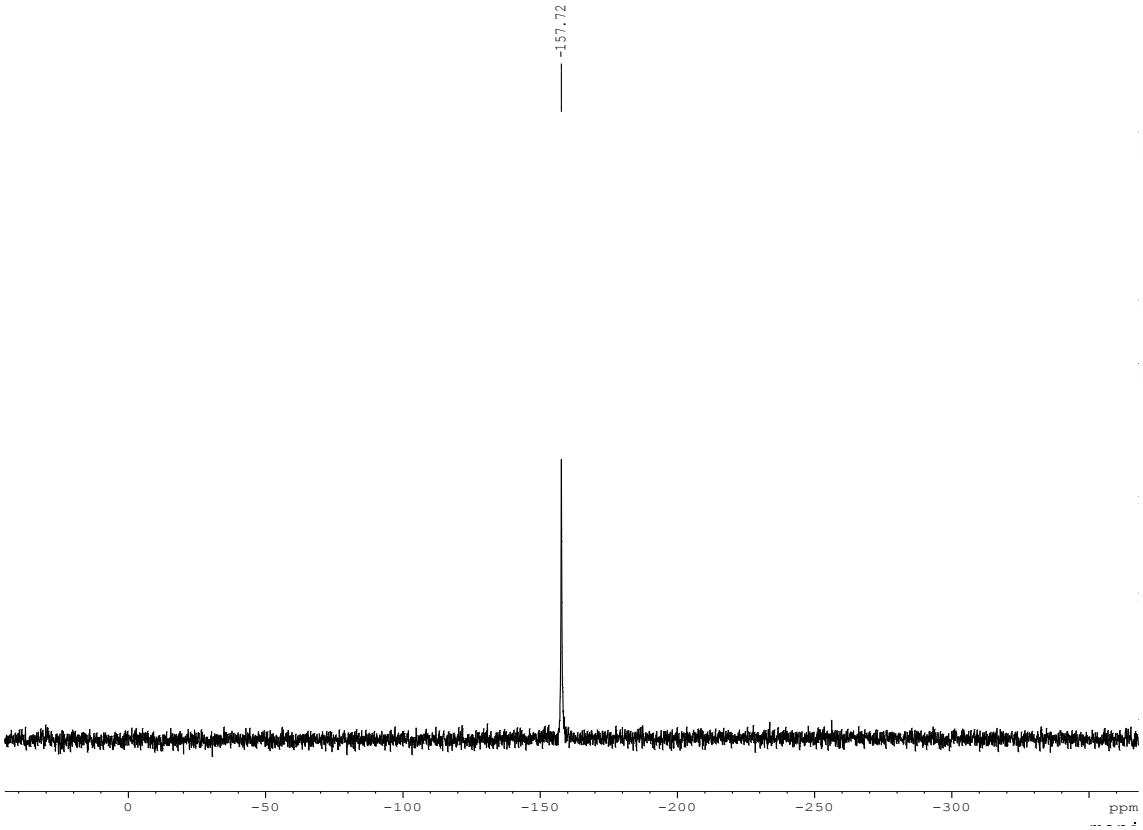


Fig. S1(c) ^{119}Sn NMR spectrum of compound **1.**

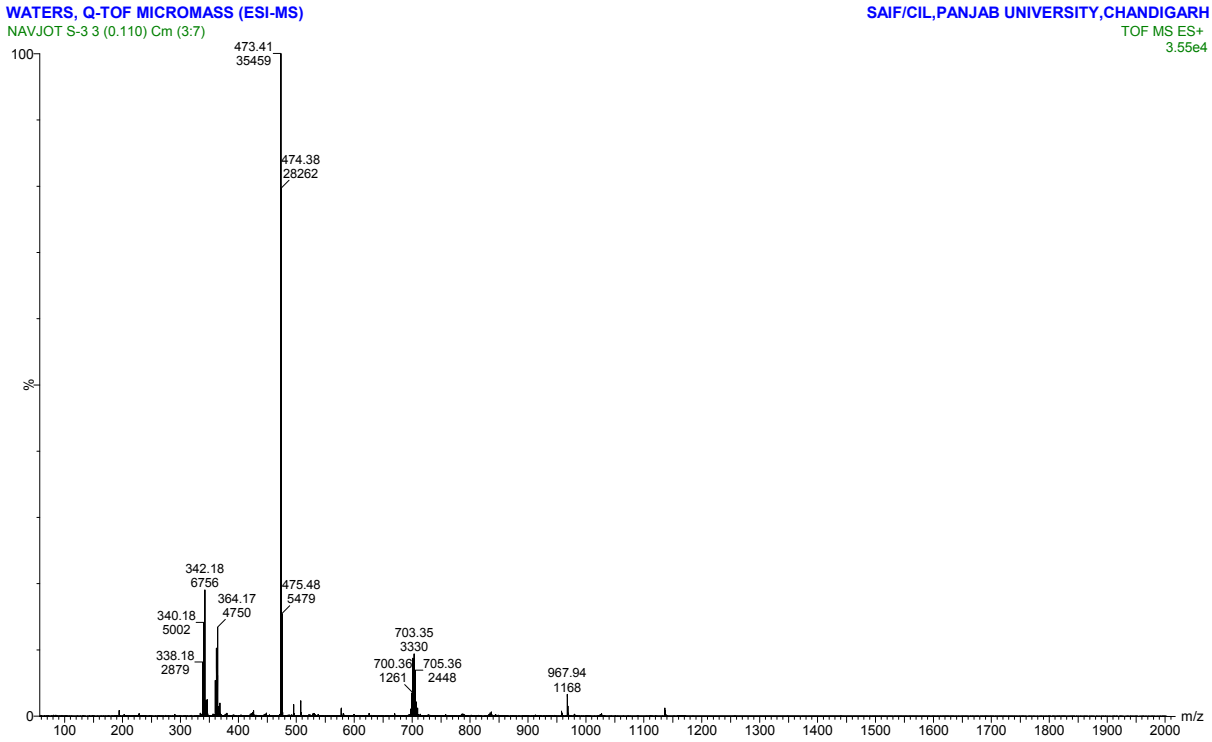


Fig. S1(d) Mass spectrum of compound **1.**

Compound 2

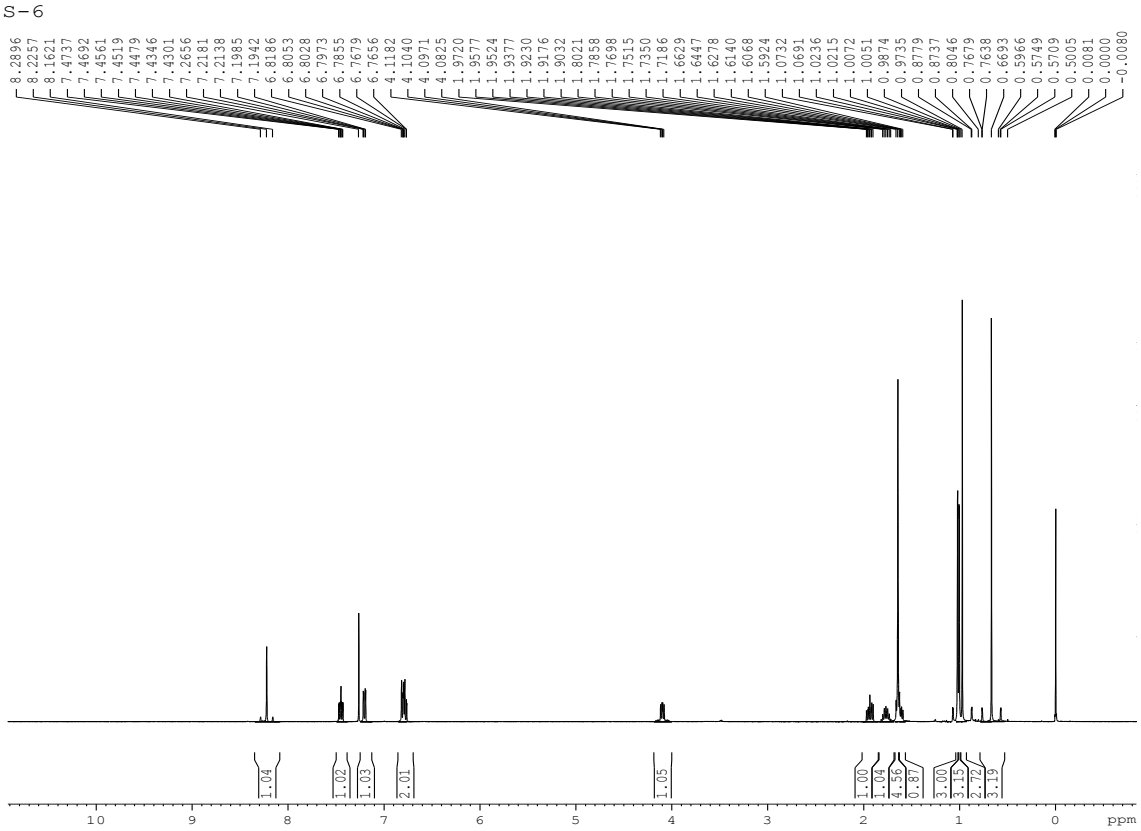


Fig. S2(a) ^{1}H NMR spectrum of compound **2**.

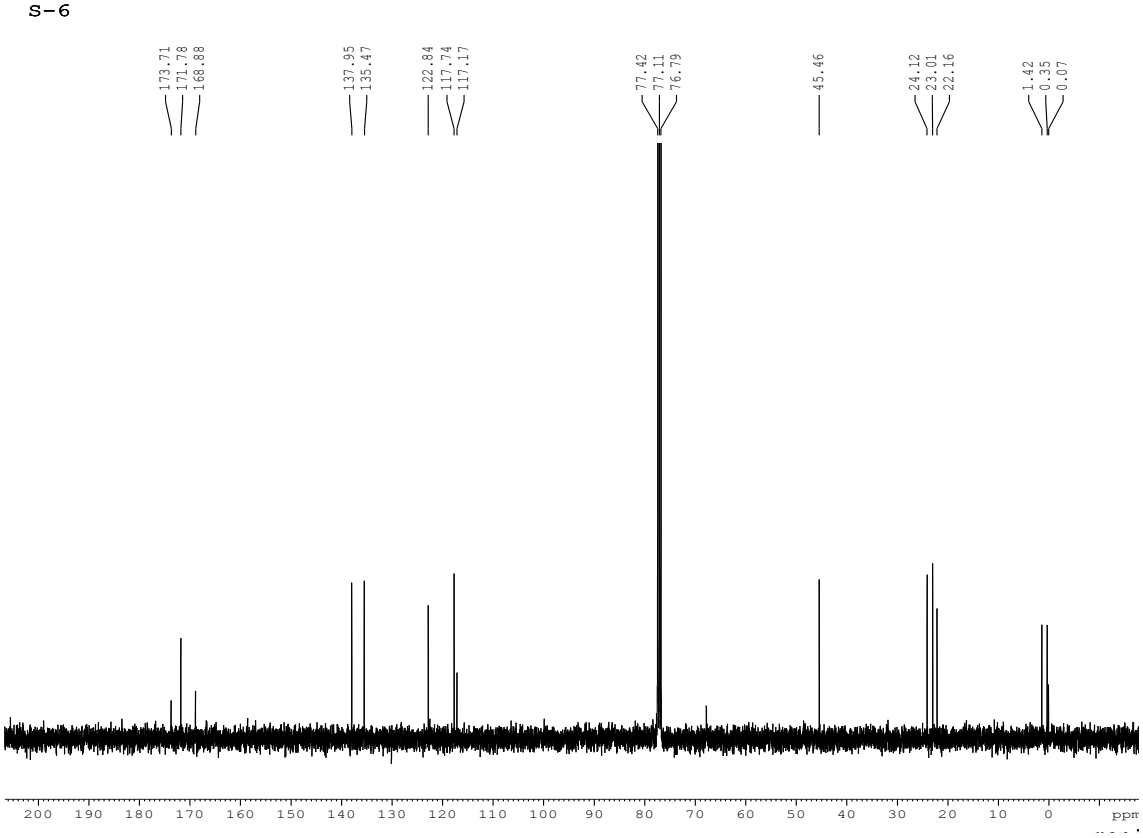


Fig. S2(b) ^{13}C NMR spectrum of compound **2**.

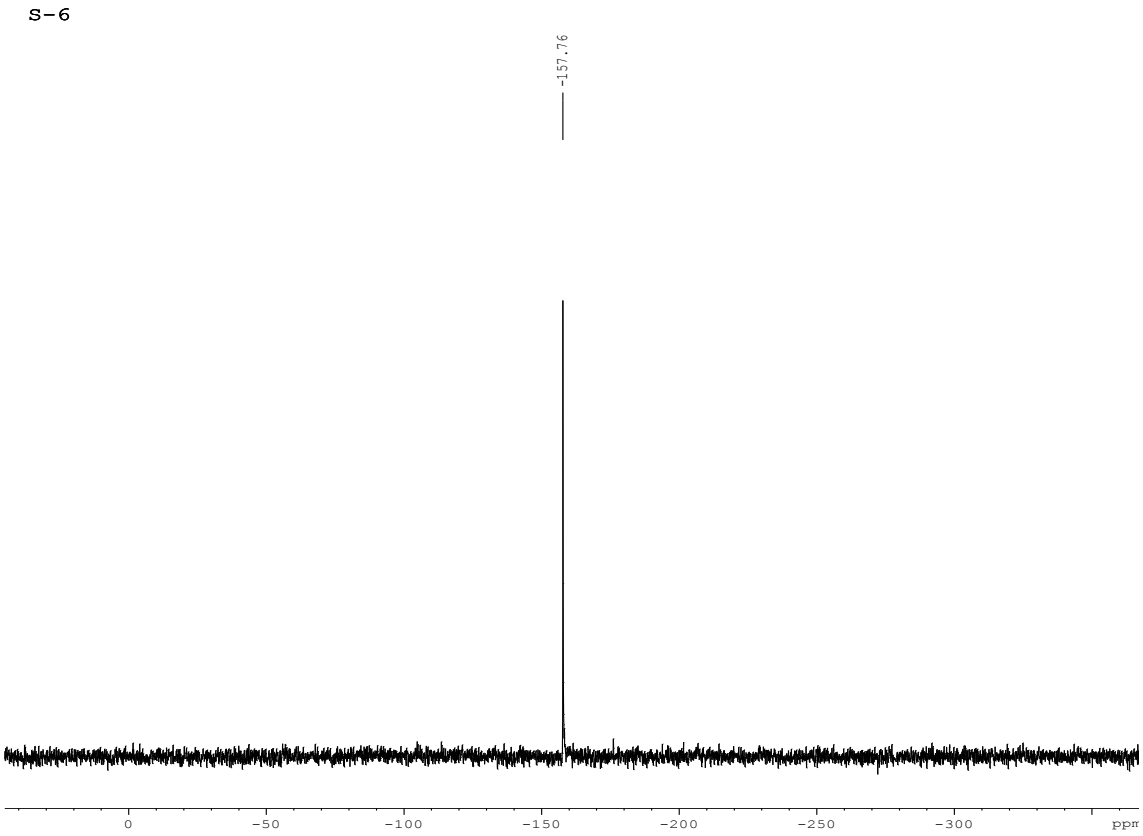


Fig S2(c) ^{119}Sn NMR spectrum of compound **2**.

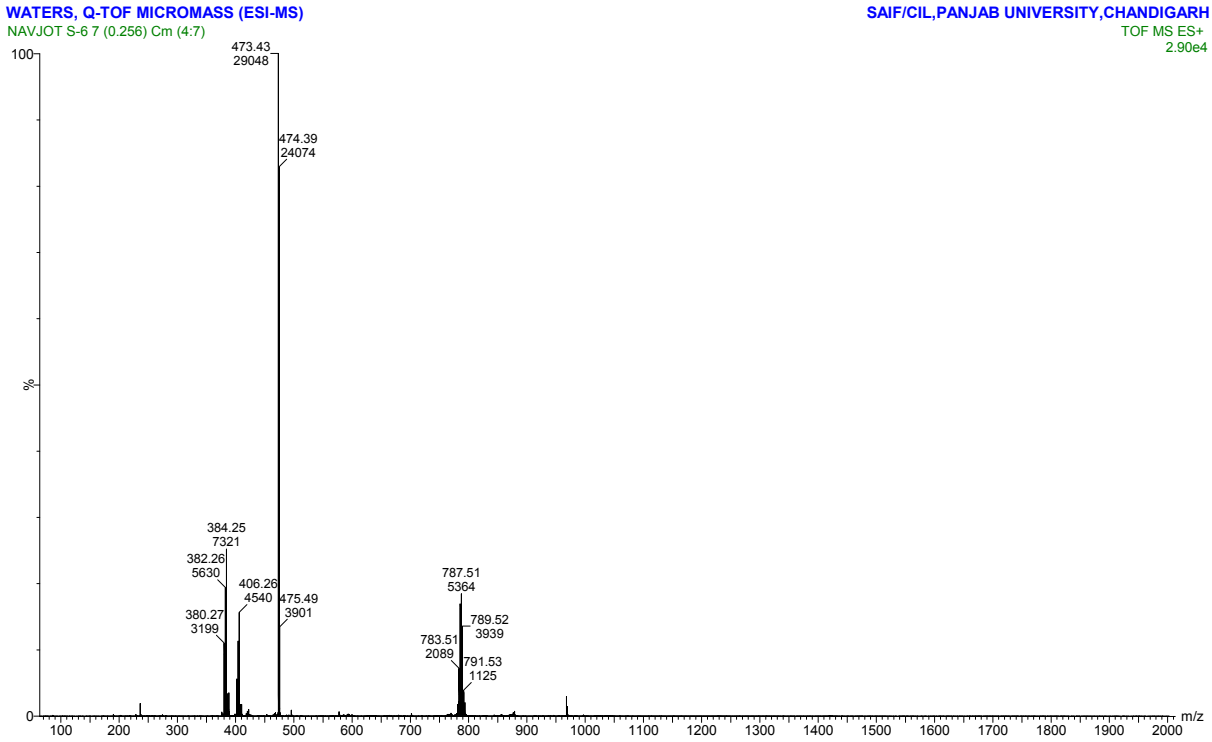


Fig. S2(d) Mass spectrum of compound **2.**

Compound 3

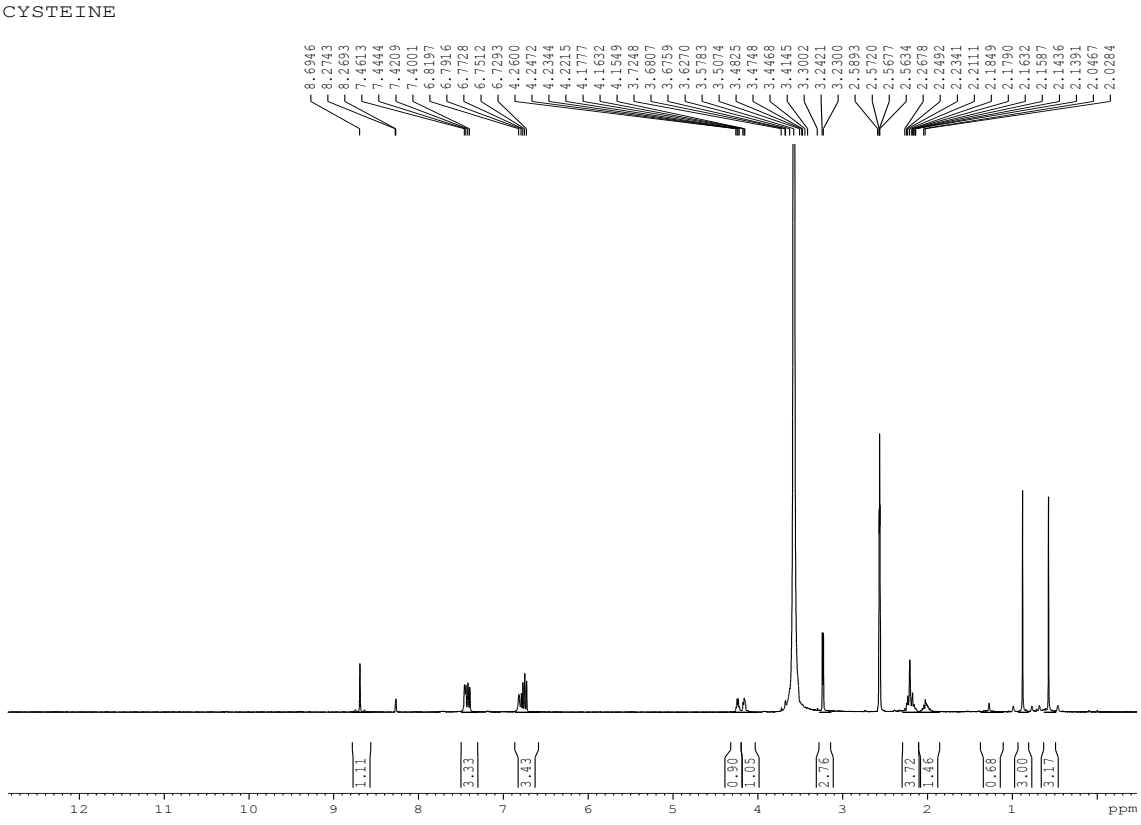


Fig. S3(a) ^{1}H NMR spectrum of compound **3**.

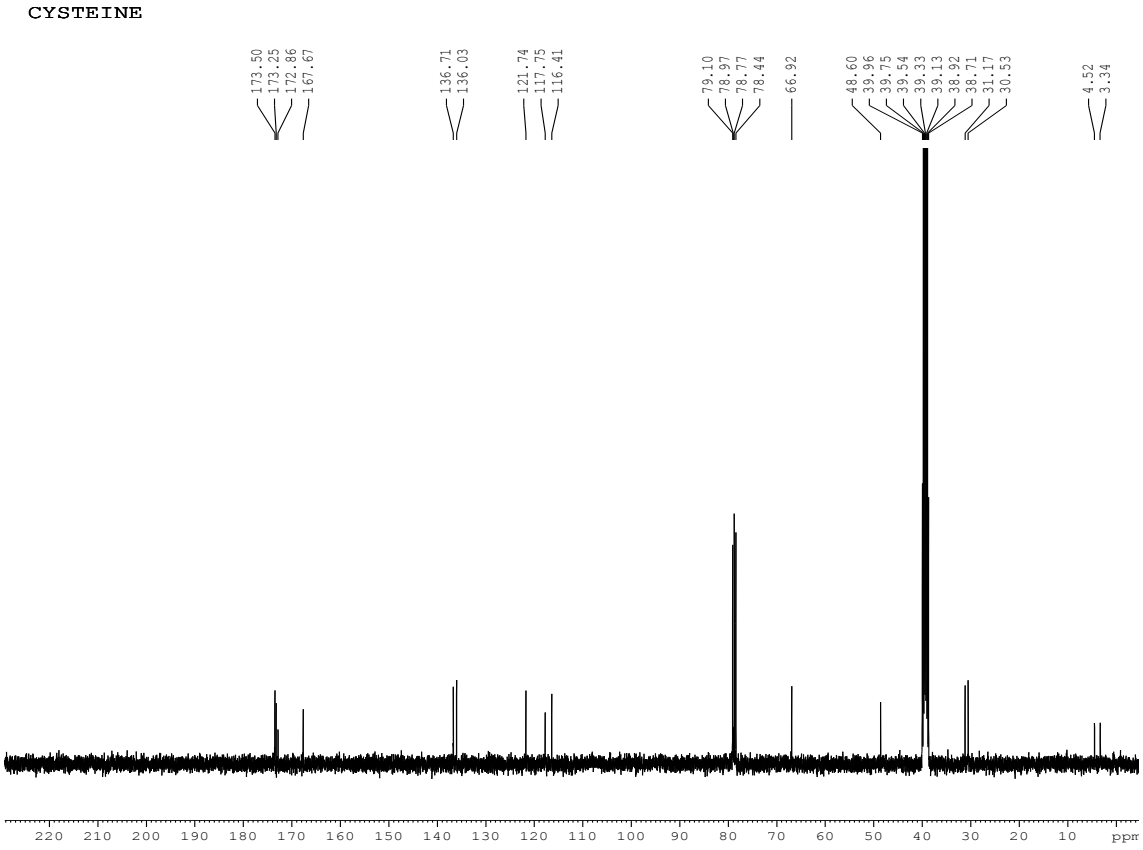


Fig. S3(b) ^{13}C NMR spectrum of compound **3**.

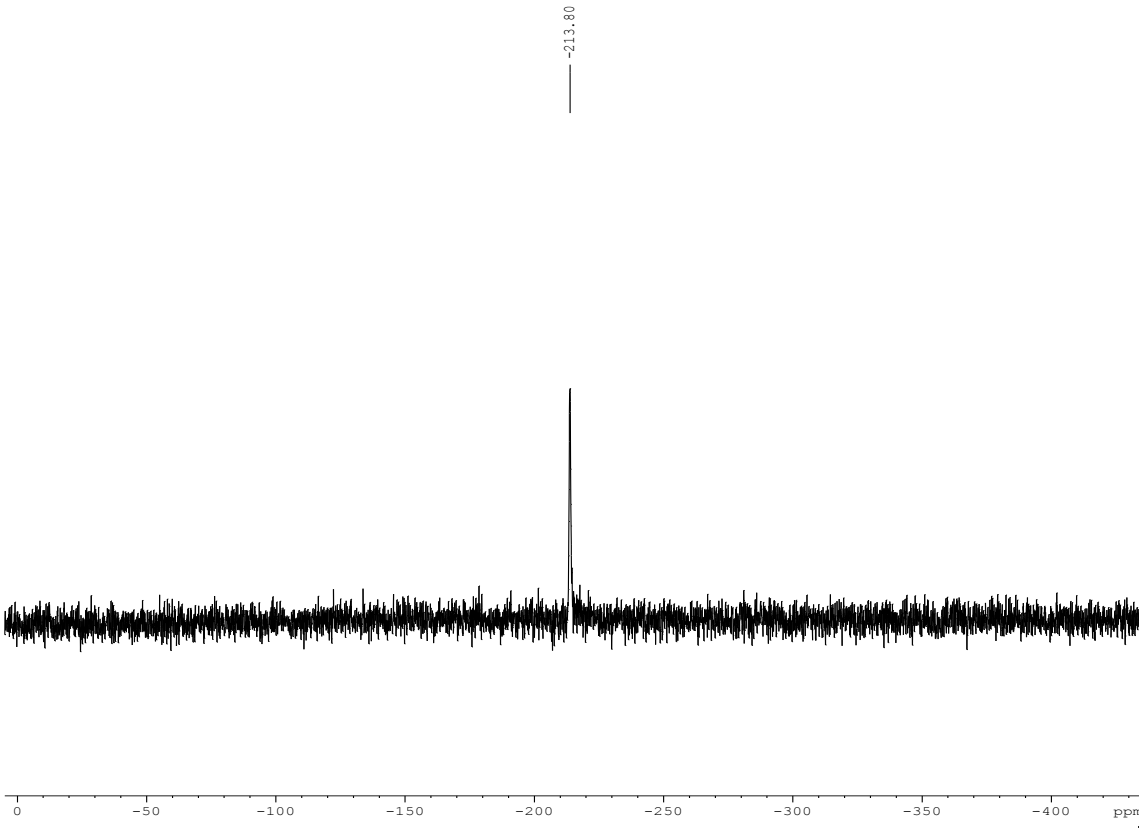


Fig. S3(c) ^{119}Sn NMR spectrum of compound **3**.

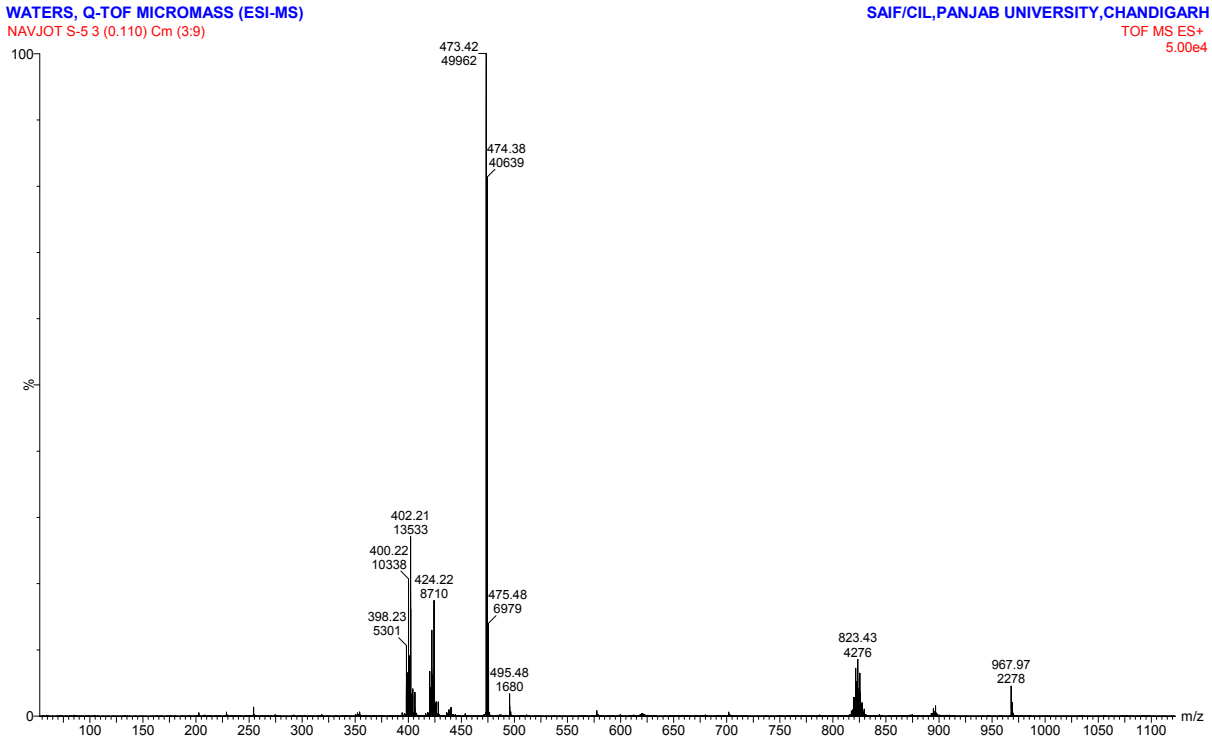


Fig. S3(d) Mass spectrum of compound **3.**

Compound 4

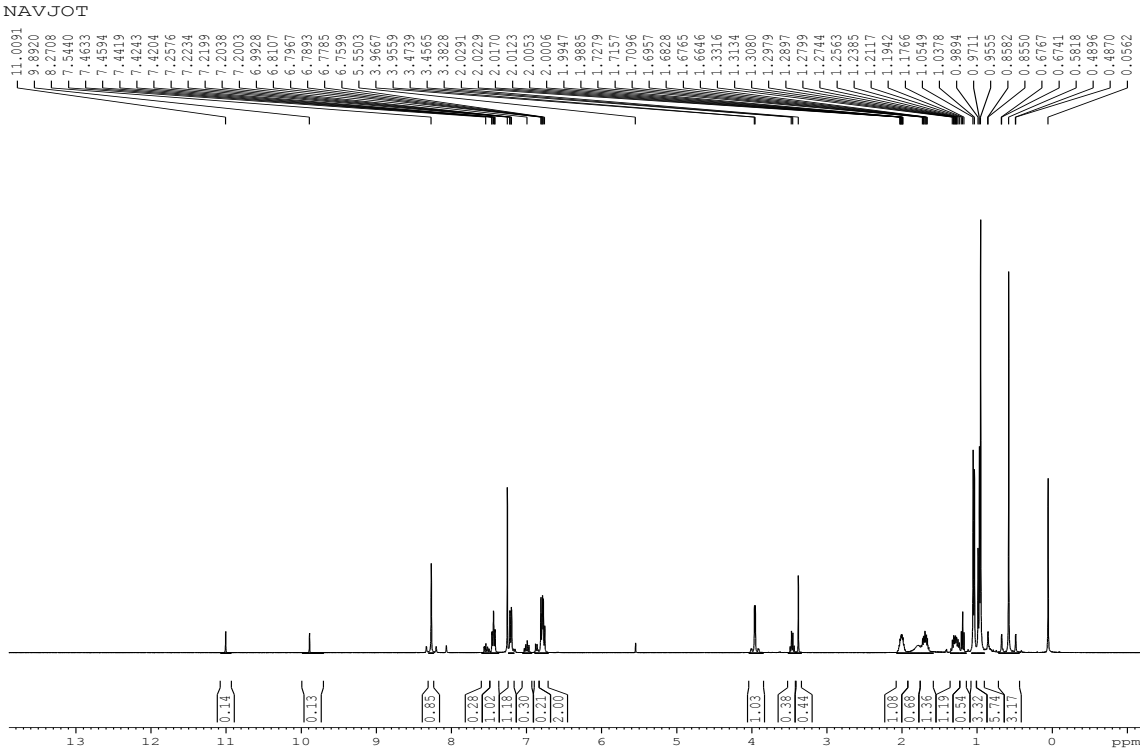


Fig. S4(a) [1]HNMR spectrum of compound **4**.

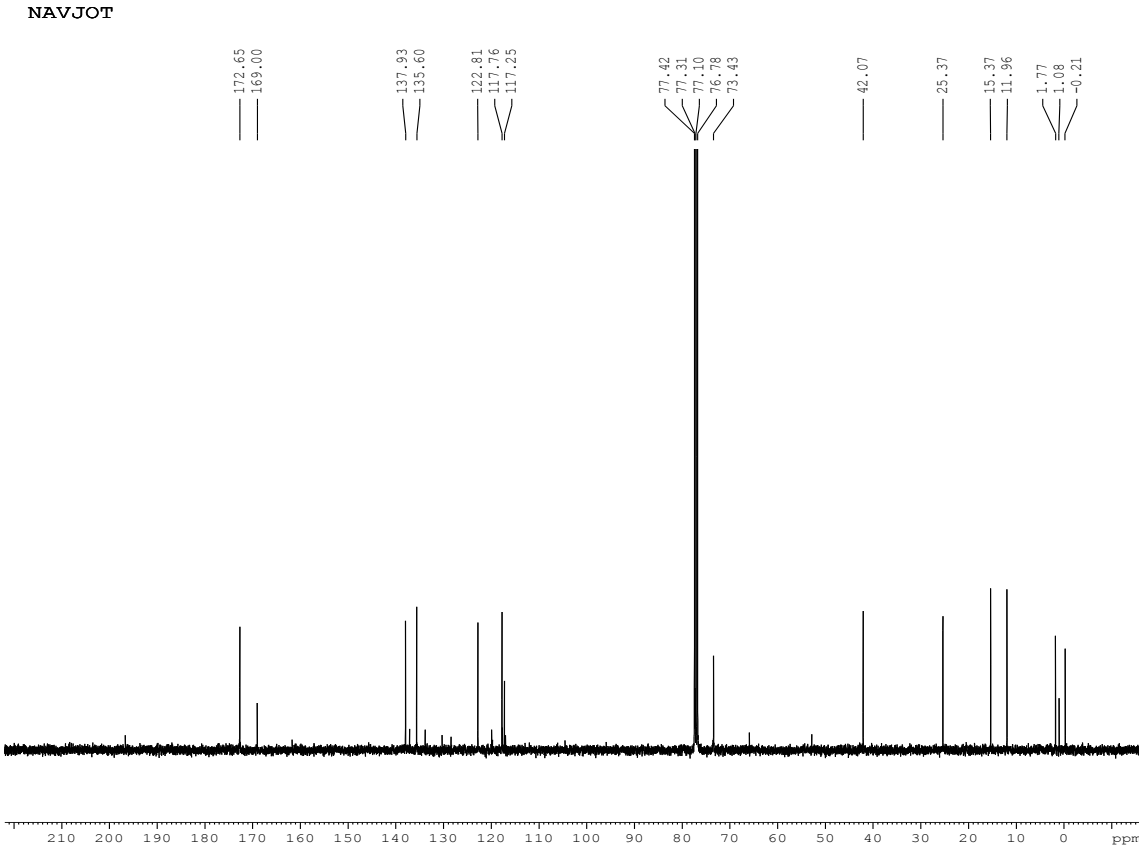


Fig. S4(b) ^{13}C NMR spectrum of compound **4**.

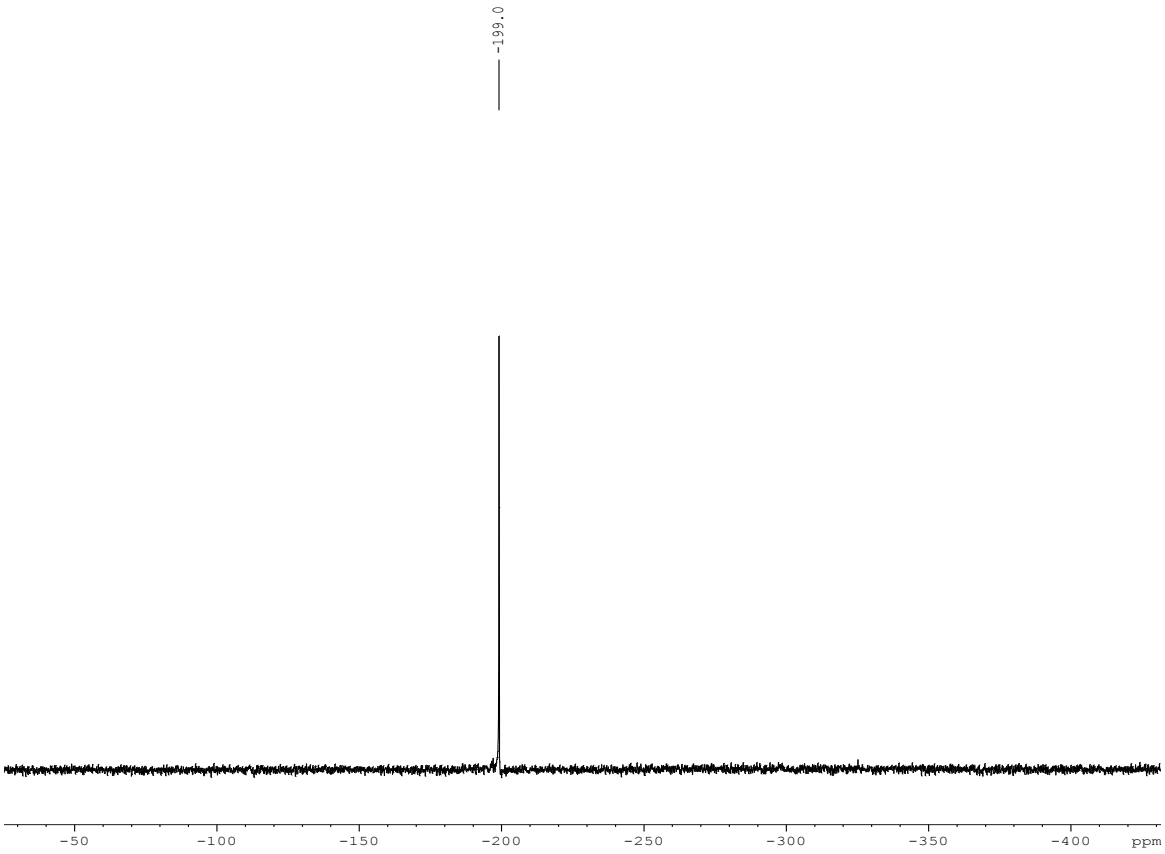


Fig. S4(c) ^{119}Sn NMR spectrum of compound **4**.

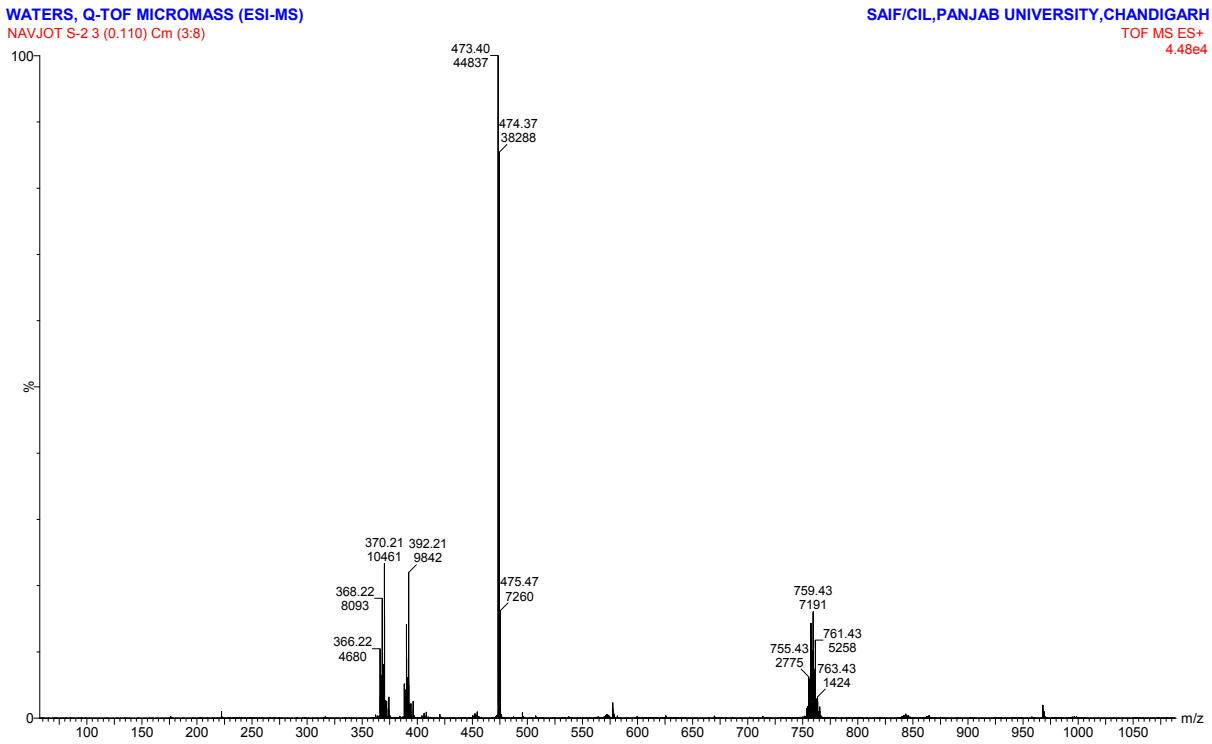


Fig. S4(d) Mass spectrum of compound **4.**

Crystal Structure

Table S1 Bond lengths and bond angles for compound 1.

Bond Angles		Bond Lengths			
Sn(1)-O(1A)	2.092(3)	O(1A)-Sn(1)-C(11A)	99.13(19)	O(1B)-Sn(2)-O(2B)	151.77(12)
Sn(1)-C(11A)	2.099(5)	O(1A)-Sn(1)-C(12A)	95.17(19)	C(12B)-Sn(2)-O(2B)	85.71(18)
Sn(1)-C(12A)	2.104(5)	C(11A)-Sn(1)-C(12A)	162.0(2)	C(11B)-Sn(2)-O(2B)	87.58(16)
Sn(1)-N(1A)	2.292(4)	O(1A)-Sn(1)-N(1A)	80.92(13)	N(1B)-Sn(2)-O(2B)	70.57(12)
Sn(1)-O(2A)	2.301(3)	C(11A)-Sn(1)-N(1A)	96.46(17)	O(1B)-Sn(2)-O(3C)	81.23(12)
Sn(1)-O(3B)	2.316(3)	C(12A)-Sn(1)-N(1A)	96.52(18)	C(12B)-Sn(2)-O(3C)	86.73(17)
O(3A)-Sn(3)	2.391(3)	O(1A)-Sn(1)-O(2A)	151.44(12)	C(11B)-Sn(2)-O(3C)	83.74(17)
N(1A)-C(7A)	1.280(6)	C(11A)-Sn(1)-O(2A)	86.96(19)	N(1B)-Sn(2)-O(3C)	162.26(11)
Sn(2)-O(1B)	2.105(3)	C(12A)-Sn(1)-O(2A)	85.65(19)	O(2B)-Sn(2)-O(3C)	126.99(11)
Sn(2)-C(12B)	2.105(5)	N(1A)-Sn(1)-O(2A)	70.65(12)	O(1C)-Sn(3)-C(12C)	94.59(18)
Sn(2)-C(11B)	2.114(5)	O(1A)-Sn(1)-O(3B)	82.65(12)	O(1C)-Sn(3)-C(11C)	103.93(19)
Sn(2)-N(1B)	2.288(4)	C(11A)-Sn(1)-O(3B)	88.50(17)	C(12C)-Sn(3)-C(11C)	157.6(2)
Sn(2)-O(2B)	2.353(3)	C(12A)-Sn(1)-O(3B)	82.54(18)	O(1C)-Sn(3)-N(1C)	81.18(13)
Sn(2)-O(3C)	2.362(3)	N(1A)-Sn(1)-O(3B)	163.38(13)	C(12C)-Sn(3)-N(1C)	103.15(17)
N(1B)-C(7B)	1.285(6)	O(2A)-Sn(1)-O(3B)	125.61(11)	C(11C)-Sn(3)-N(1C)	92.11(17)
Sn(3)-O(1C)	2.065(3)	O(1B)-Sn(2)-C(12B)	97.68(19)	O(1C)-Sn(3)-O(2C)	149.51(12)
Sn(3)-C(12C)	2.110(5)	O(1B)-Sn(2)-C(11B)	96.29(17)	C(12C)-Sn(3)-O(2C)	83.95(17)
Sn(3)-C(11C)	2.117(5)	C(12B)-Sn(2)-C(11B)	161.7(2)	C(11C)-Sn(3)-O(2C)	86.25(18)

Sn(3)-N(1C)	2.271(4)	O(1B)-Sn(2)-N(1B)	81.22(13)	N(1C)-Sn(3)-O(2C)	69.63(12)
Sn(3)-O(2C)	2.379(3)	C(12B)-Sn(2)-N(1B)	98.17(18)	O(1C)-Sn(3)-O(3A)	79.87(12)
N(1C)-C(7C)	1.299(6)	C(11B)-Sn(2)-N(1B)	95.63(17)	C(12C)-Sn(3)-O(3A)	86.97(18)

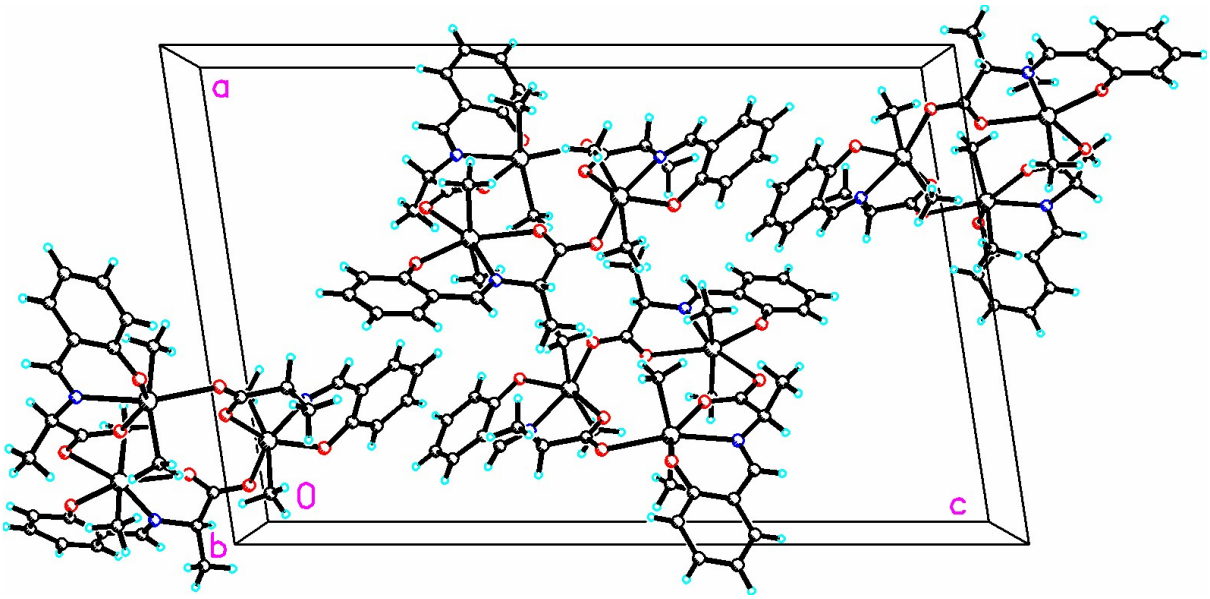


Fig. S5 Unit cell packing of compound 1. There are four independent molecules per unit cell i.e. Z = 4. View is generated by ORTEP.

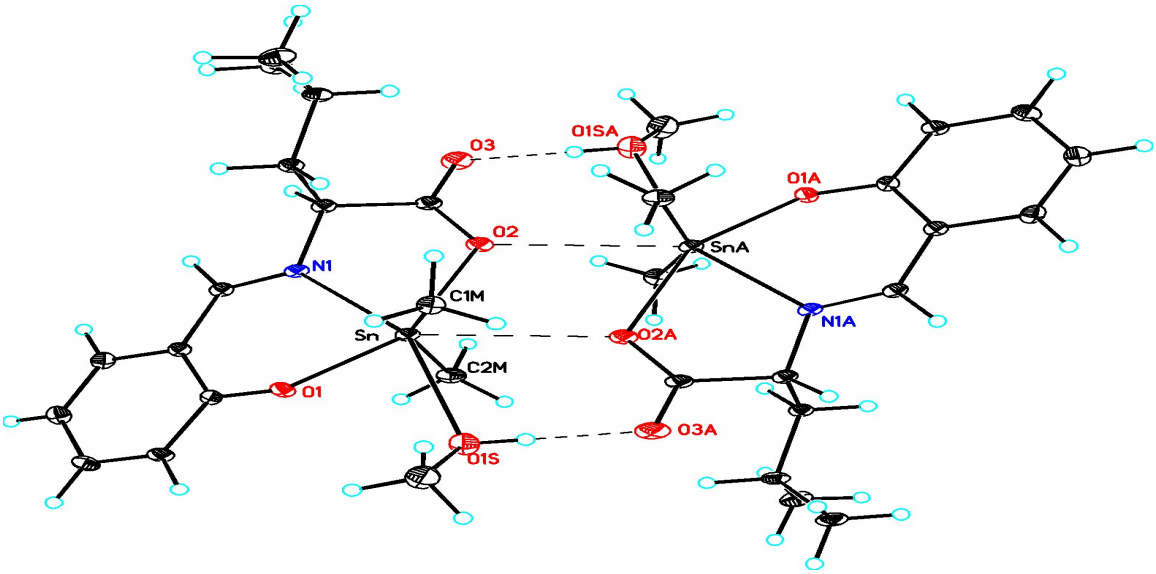


Fig. S6 Intramolecular hydrogen bonding between two independent molecules of 2. H-bonds are formed between O(3)…H(1SA), O(3A)…H(1S) as well as intermolecular coordination of O(3), O(3A) towards Sn and Sn(A).

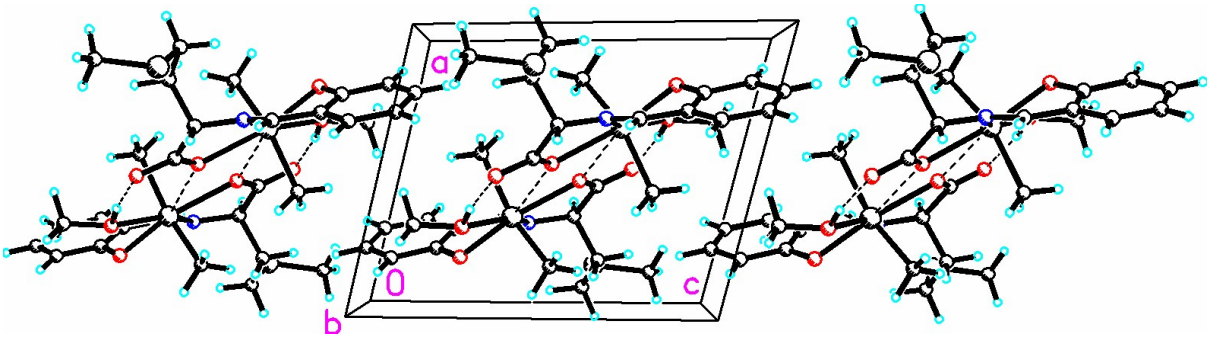


Fig. S7 Unit cell packing diagram of 2 revealing two intramolecularly hydrogen bonded monomeric units bonded to each other.

Table S2 Bond lengths and bond angles for compound 2.

Bond Lengths		**Bond Angles**			
Sn-O(1)	2.094(4)	O(1)-Sn-C(1M)	96.1(2)	C(1M)-Sn-O(1S)	80.9(2)
Sn-C(1M)	2.100(6)	O(1)-Sn-C(2M)	99.3(2)	C(2M)-Sn-O(1S)	81.9(2)
Sn-C(2M)	2.113(6)	C(1M)-Sn-C(2M)	152.2(3)	N(1)-Sn-O(1S)	152.20(17)
Sn-N(1)	2.244(4)	O(1)-Sn-N(1)	80.26(16)	O(2)-Sn-O(1S)	136.40(16)
Sn-O(2)	2.321(4)	C(1M)-Sn-N(1)	106.0(2)	C(7)-N(1)-C(8)	118.5(5)
Sn-O(1S)	2.572(5)	C(2M)-Sn-N(1)	99.4(2)	C(7)-N(1)-Sn	124.2(4)
O(1)-C(1)	1.313(7)	O(1)-Sn-O(2)	151.43(15)	C(8)-N(1)-Sn	116.4(4)
O(2)-C(9)	1.275(7)	C(1M)-Sn-O(2)	89.8(2)	C(1S)-O(1S)-Sn	123.8(5)
O(3)-C(9)	1.235(7)	C(2M)-Sn-O(2)	87.7(2)	C(1S)-O(1S)-H(1S)	109.5
N(1)-C(7)	1.279(8)	N(1)-Sn-O(2)	71.25(16)	Sn-O(1S)-H(1S)	104.2
N(1)-C(8)	1.472(7)	O(1)-Sn-O(1S)	72.17(16)	N(1)-C(8)-C(9)	109.1(5)

Photophysical studies

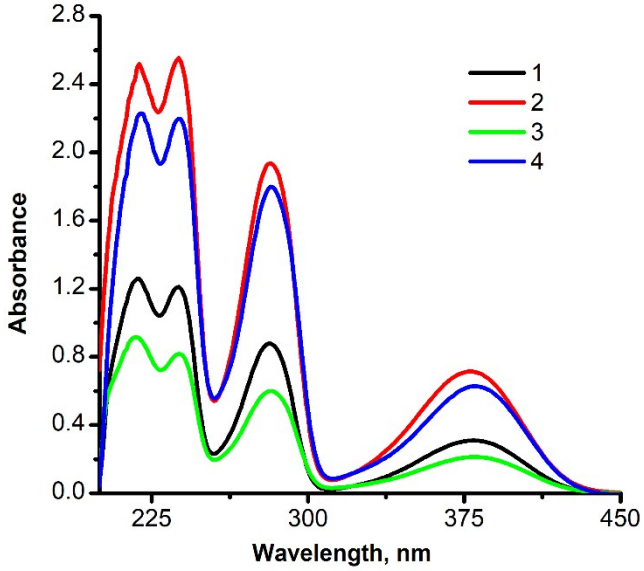


Fig S8. UV-visible spectra of 1-4 (0.05 mM) in methanol.

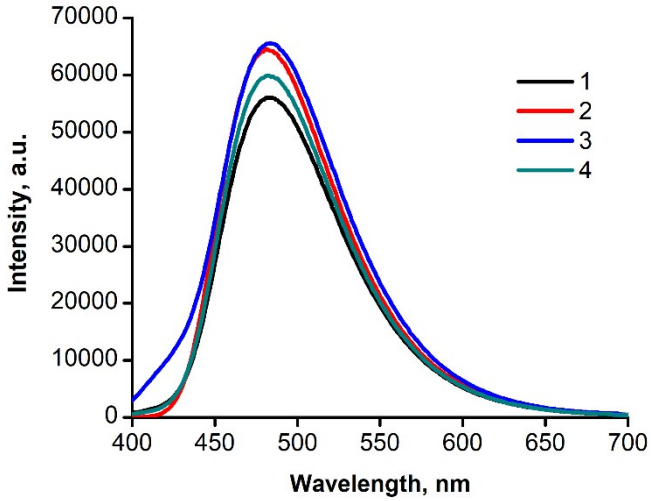


Fig S9. Fluorescence spectra of 1-4 (0.05 mM) in methanol.

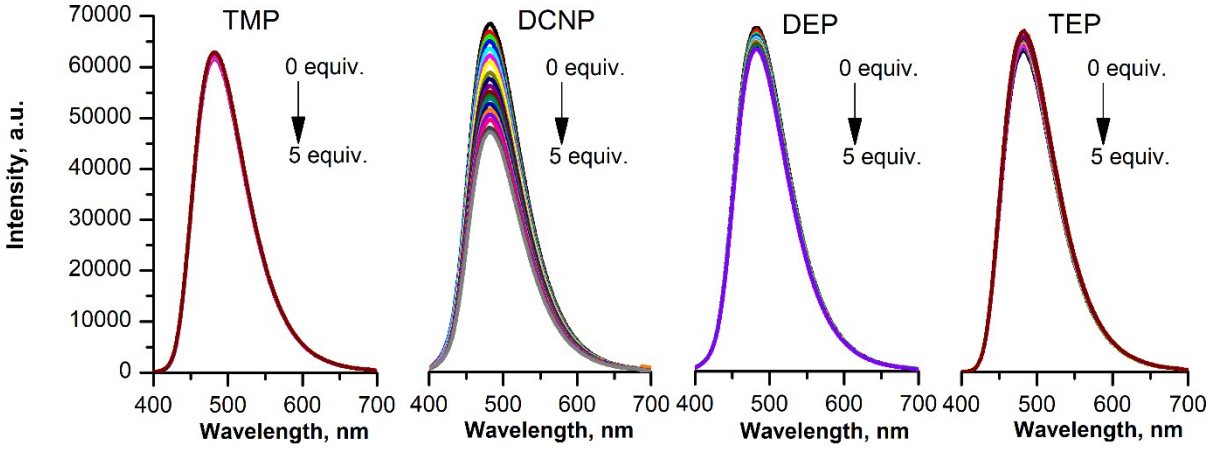


Fig. S10 Fluorescence emission of compound 2 (0.05 mM) with TMP, DCNP, DEP and TEP (5 mM, each).

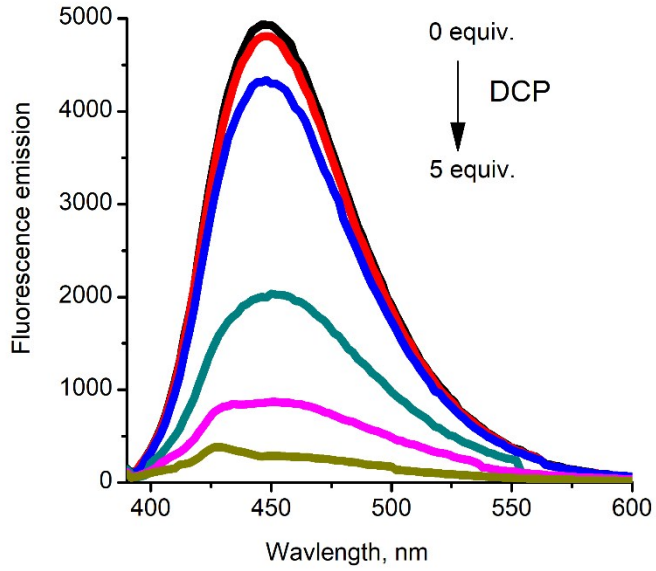


Fig. S11 Spectrofluorometric titration of 2 (0.758 µM) with DCP (100 mM)

Quantum Yield

Quantum yield was calculated according to the following equation.

$$QY_x = QY_{ST}\frac{F_x A_{ST} \eta_X^2}{F_{ST} A_X \eta_{ST}^2}$$

F is the integral photon flux, A is the absorption factor, η is the refractive index of the solvent and QY is the quantum yield. The index X denotes the sample, and the index ST denotes the standard. Anthracene in ethanol was used as the reference (QY = 0.27).

Fluorescence Lifetime

Fluorescence life-time was calculated by using the following equation.

$$\text{Fluorescence life-time } (\tau) = (B_1T_1^2 + B_2T_2^2)/(B_1T_1 + B_2T_1)$$

Where B_1, B_2, T_1 and T_2 were parameters calculated from fitted fluorescence decay data for each individual system. The values of B_1, B_2, T_1 and T_2 are given below.

Compound	Parameters (B_1, B_2, T_1 and T_2)
2 in the presence of DCP	$B_1 = 2.266259 \times 10^{-2}$, $B_2 = 6.884229 \times 10^{-4}$ $T_1 = 25.28073$, $T_2 = 133.1196$
2	$B_1 = 1.487165 \times 10^{-2}$, $B_2 = 2.391968 \times 10^{-4}$ $T_1 = 26.4969$, $T_2 = 230.6804$

Mechanism for interaction

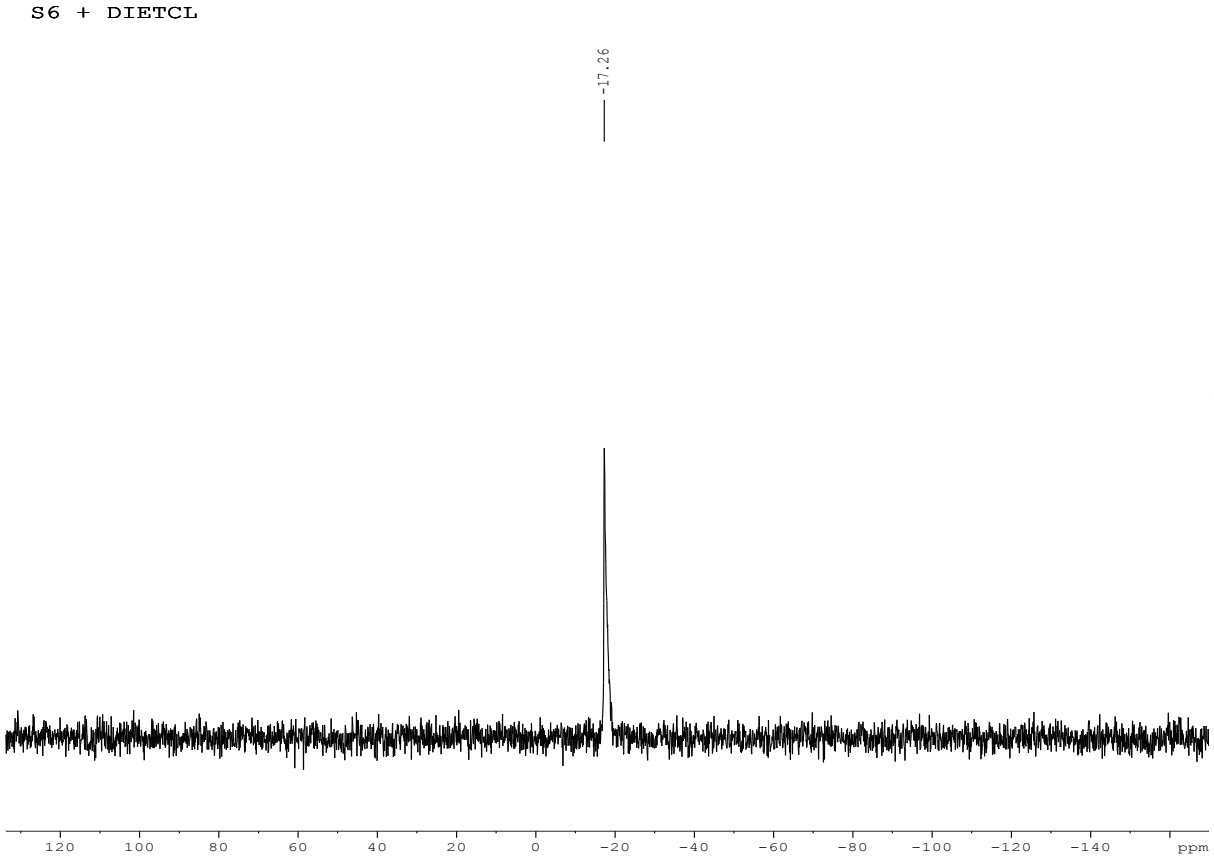


Fig. S12 ^{119}Sn NMR spectrum of compound **2** with addition of DCP.

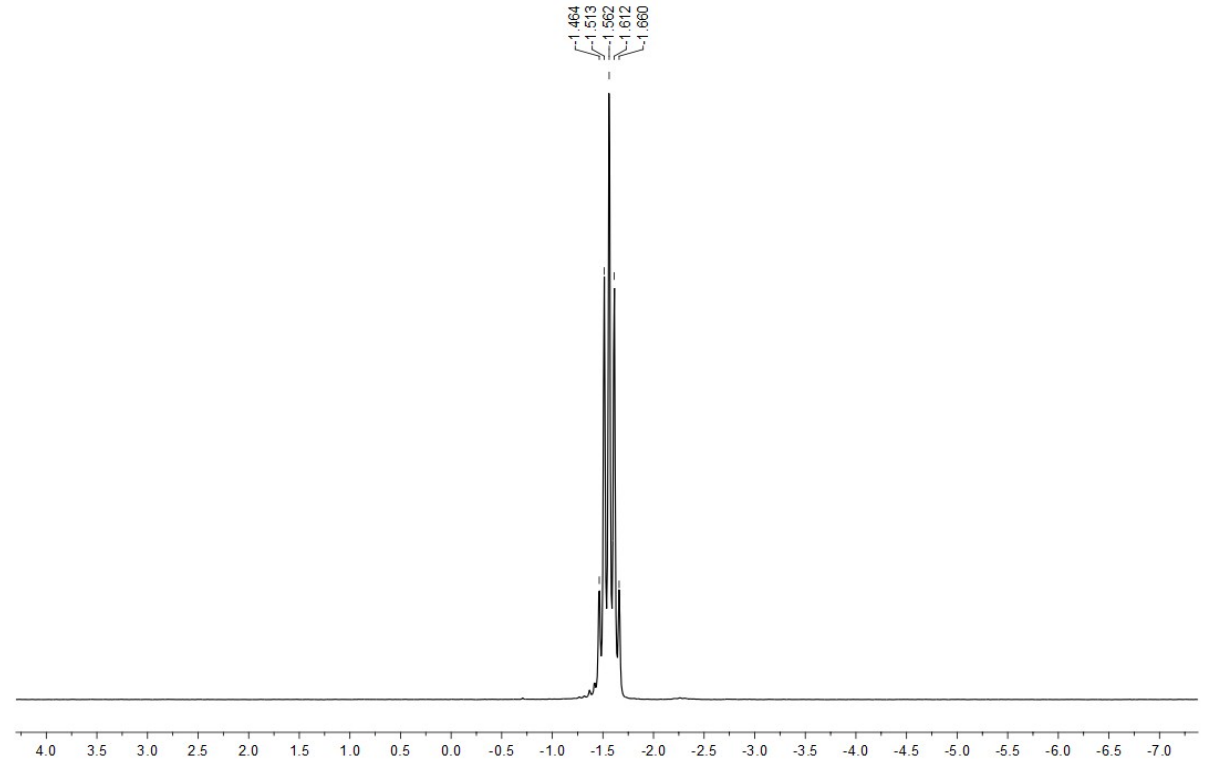


Fig. S13 ^{31}P NMR spectrum of diethyl chlorophosphate (DCP).

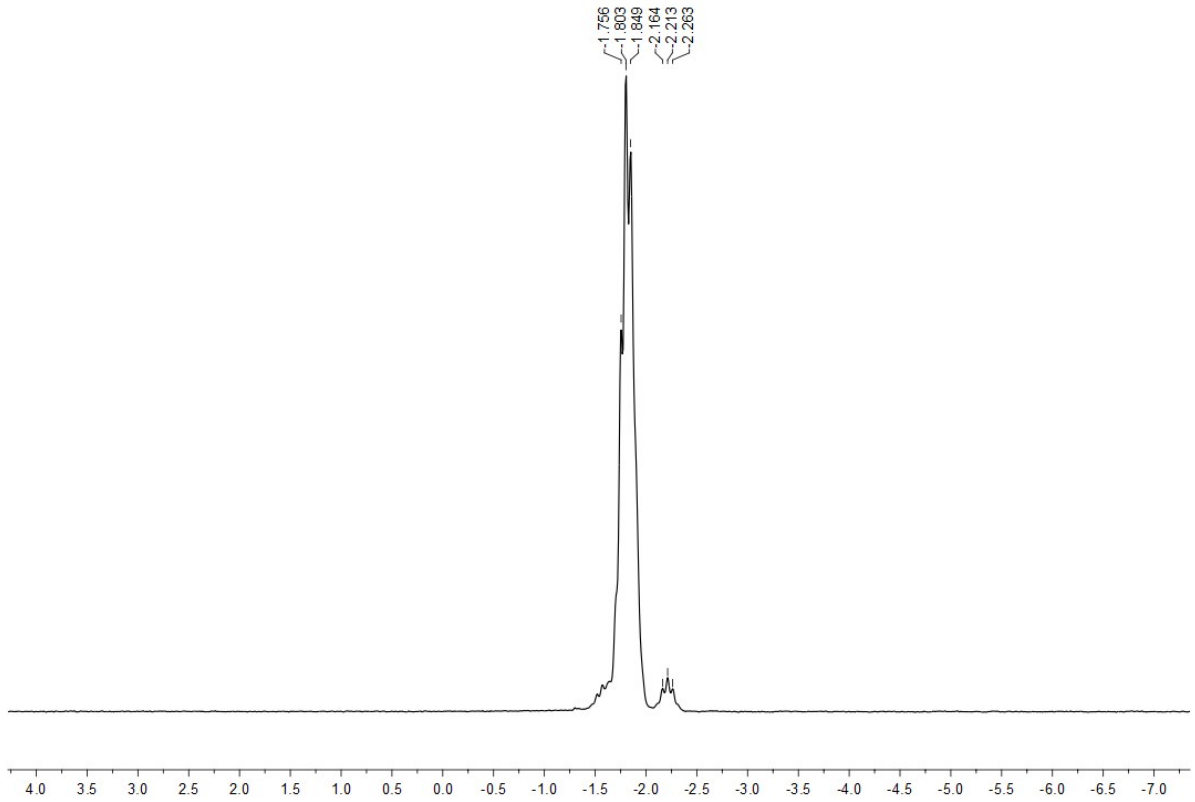


Fig. S14 ^{31}P NMR spectrum of compound 2 in the presence of 3 equivalents of DCP.

Table S3 Mass fragmentation of spectrometric data for 2:DCP mixture.

S.No	Fragment(molecular mass)	m/z(MS)
1	$C_{19}H_{31}ClNO_6PSn$	554
2	$C_{15}H_{21}ClNO_4PSn$	464.9
3	$C_{14}H_{18}ClNO_4PSn_3^{\bullet}$	449.9
4	$C_9H_{11}ClNOSn^{\bullet}$	303.9
5	$C_9H_{11}NOSn^{2\bullet}$	268.9
6	C_2H_7ClOSn	201.9
7	$C_7H_7^{\bullet+}$	91
8	$ClOP_3^{\bullet}$	81.9

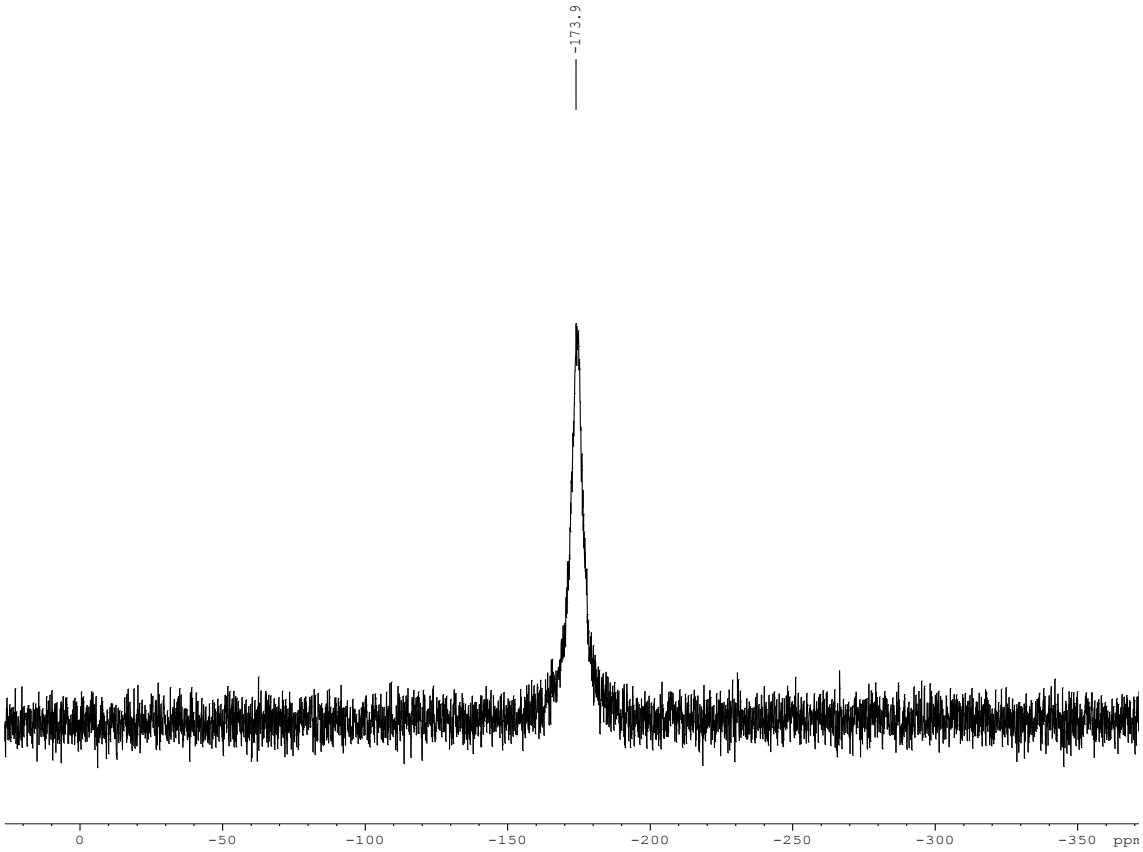


Fig. S15 ^{119}Sn NMR Spectrum of a mixture of **2** and DCNP.

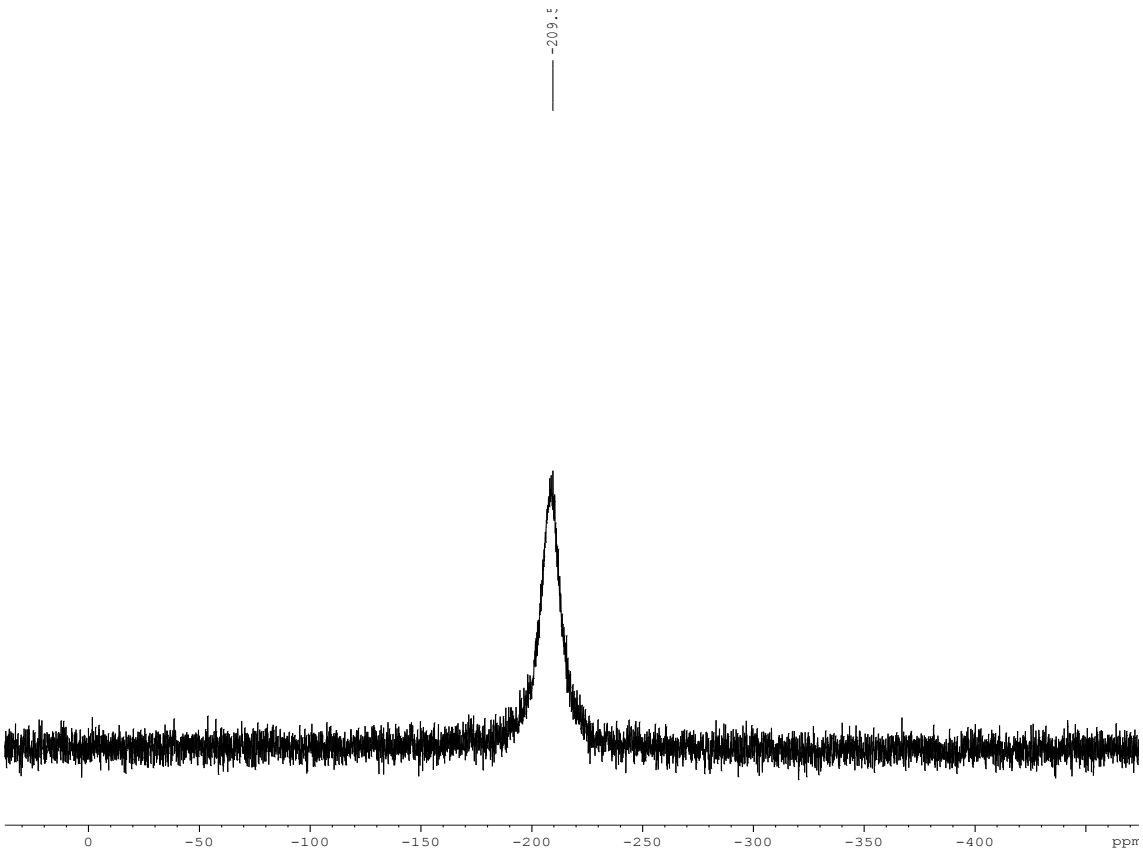


Fig. S16 ^{119}Sn NMR Spectrum of a mixture of **2** and DEP.

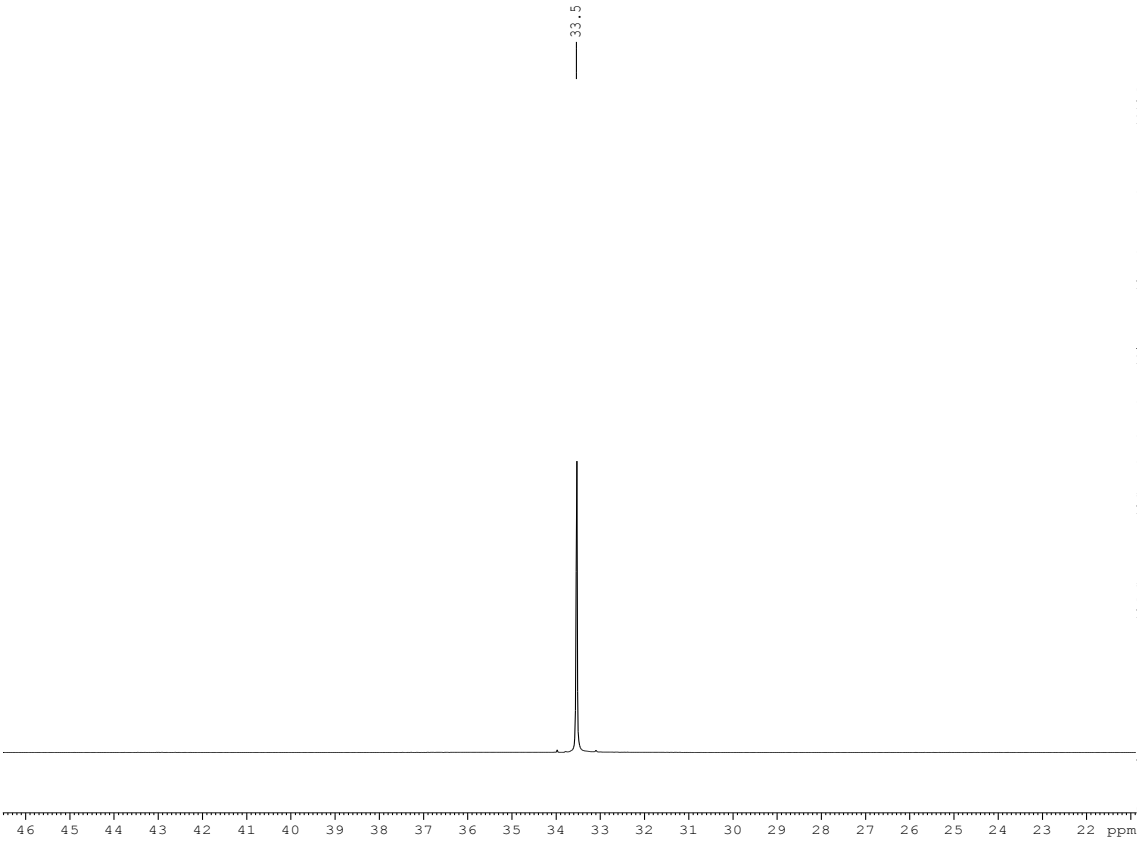


Fig. S17 ^{31}P NMR spectrum of compound **2** in the presence of 3 equivalents of DEP.

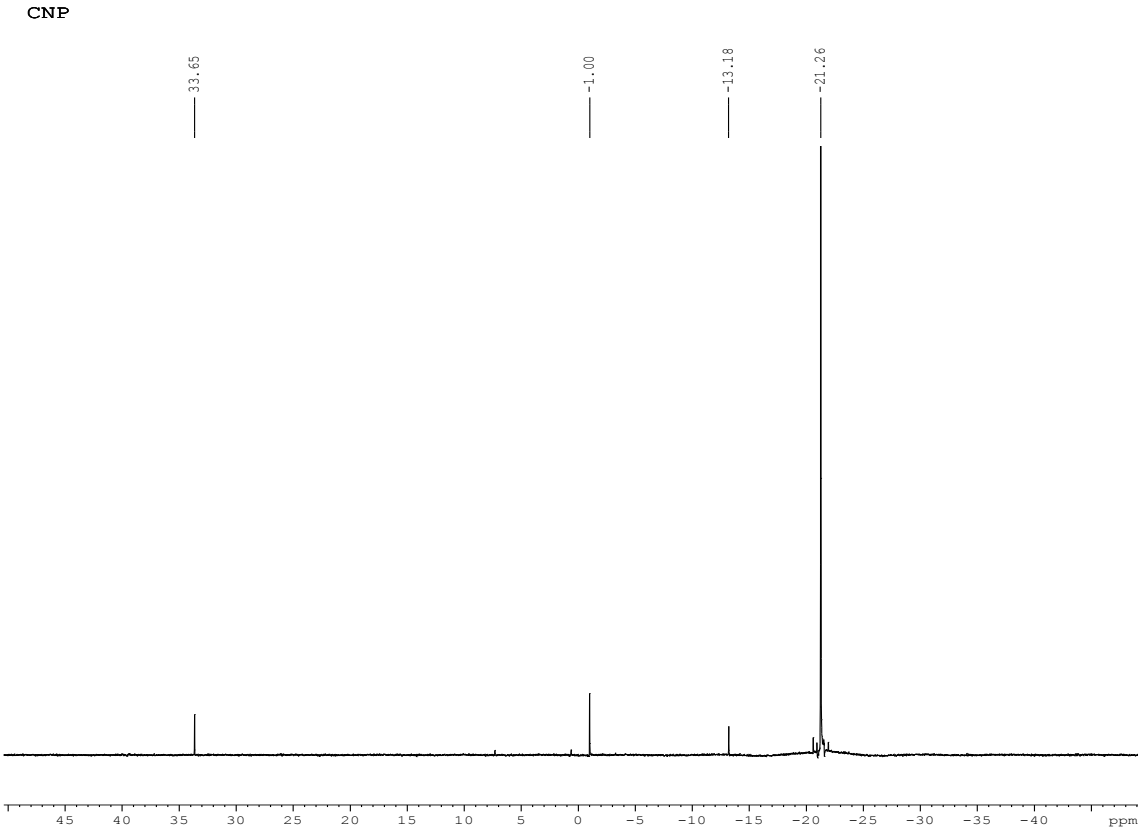


Fig. S18 ^{31}P NMR Spectrum of DCNP.

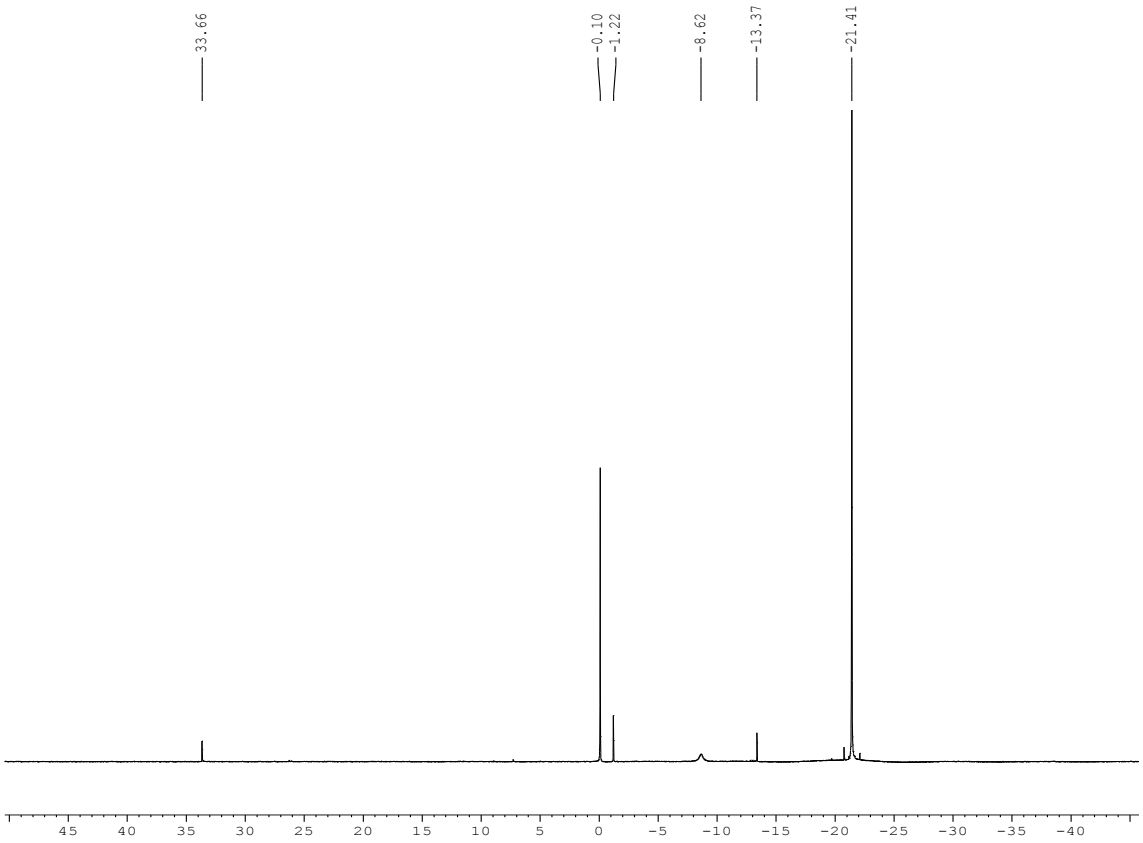


Fig. S19 ^{31}P NMR Spectrum of a mixture of **2** and DCNP.

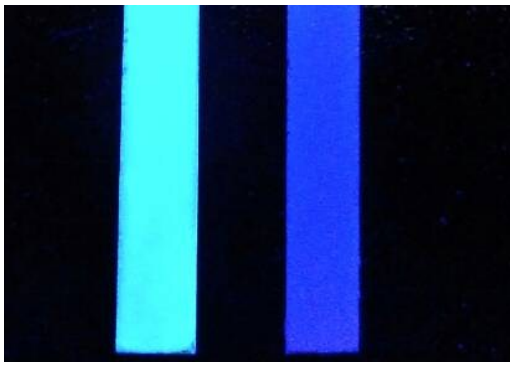
Application of devices in real samples

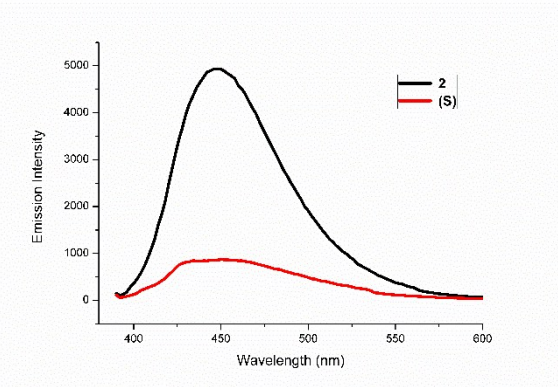
(a) Detection of DCP in soil and water samples

A soil sample weighing 10 g taken was spiked with a 1 mL of neat DCP. Thereafter, DCP was then leached out by stirring in methanol. After filtration, the filtrate was taken as a stock sample **(S)** of DCP of which 1 mL was added in methanolic solution of **2** (0.758 μM), thereafter, fluorescence emission was recorded. The gradual quenching occurring parallel to the previously performed titration with methanolic solution of DCP (100 mM) demonstrated the use of compound **2** as real time working probe for detection of DCP. The SiO_2@Al coated with fluorescent probe **2** when dipped in **S,** lost its fluorescence emission when placed under UV-lamp **(Fig 13)**.

(b) Detection of DCP in water samples by using fluorescent SiO_2@Al strips

To detect the presence of DCP in water. A 10-mL water sample was spiked with 1 mL of neat DCP in a 50-mL beaker. Afterwards, fluorescent SiO_2@Al strip were dipped into the analyte solution. The quenched fluorescence of the exposed strip **(Fig 14)** depicts successful applicability of portable strips for the detection of DCP in water samples.





(a) **(b)**

Fig. S20 The determination of DCP in soil samples by using (a) probe 2 coated SiO_2@Al fluorescent strips, (b) fluorescence of leached methanolic solution.

Fig. S21 Setup for the vapour phase recognition of DCP via **2@SiO_2@Al** strips.