Organotin esterification of (E)-3-(3-fluoro-phenyl)-2-(4-chlorophenyl)-2-propenoic acid: synthesis, spectroscopic characterization and in vitro biological activities. Crystal structure of [Ph$_3$Sn(OC(O)C(4-ClC$_6$H$_4$) = CH(3-FC$_6$H$_4$))]

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Abstract

Nine organotin esters, Me$_2$SnL$_2$ **1**, Me$_3$SnL **2**, n-Bu$_2$SnL$_2$ **3**, n-Bu$_3$SnL **4**, Ph$_3$SnL **5**, (PhCH$_2$)$_2$SnL$_2$ **6**, [(Me$_2$SnL)$_2$O]$_2$ **7**, Et$_2$SnL$_2$ **8** and n-Oct$_2$SnL$_2$ **9**, of (E)-3-(3-fluorophenyl)-2-(4-chlorophenyl)-2-propenoic acid, **HL** have been synthesized and characterized by elemental analysis, IR, Multinuclear NMR (^{1}H, ^{13}C and ^{119}Sn) and mass spectrometry. The geometry around the tin atom has been deduced and compared both in solution and solid states. The crystal structure of compound **5** has been determined by X-ray single crystal analysis, which shows a tetrahedral geometry around the tin atom with space group $P\bar{1}$. These compounds have also been screened for bactericidal, fungicidal activities and cytotoxicity data.
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Keywords: Organotin(IV) complexes; Multinuclear NMR; Mass spectrometry; X-ray structure; Antifungal activity; Antibacterial activity

1. Introduction

Organometallic compounds comprise an important class of antitumor agents [1]. Among the organometallic compounds organotin carboxylates have been shown increasing interest due to their activity against various types of cancer. In fact many of the di-n-butyltin(IV), tri-n-butyltin(IV) and triphenyltin (IV) complexes display interesting antitumor activities. Recent work also reveals higher antitumor activities for various di- and tri-organotin fluoro-substituted carboxylates than their non-fluorinated analogues [2]. Another aspect of major interest in organotin carboxylates is of their structural diversity. Beside diorganotin dicarboxylates, triorganotin esters also show rich and diverse structural chemistry. For example the structures of triorganotin carboxylates range from a discrete form to polymer chain as shown in Scheme 1 [3–5]. Keeping in view the structural and biological diversity of organotin(IV) carboxylates and in connection with our interest in coordination chemistry of organotin compounds with different carboxylic acids [6–10], here we present the synthesis, characterization and in vitro biological

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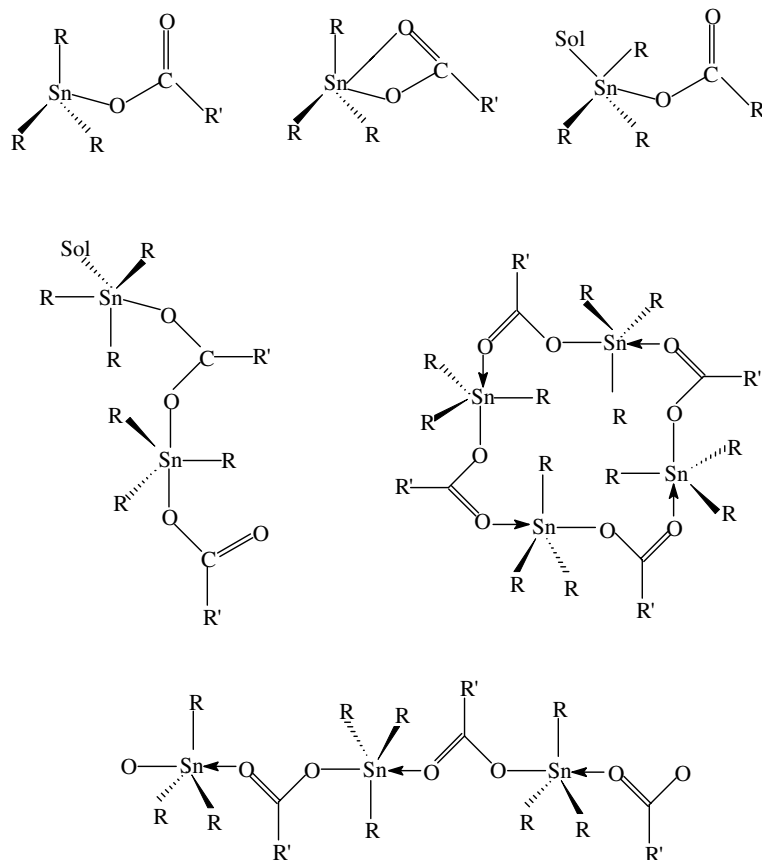
Scheme 1. The various structural forms of triorganotin carboxylates.

activity of a carboxylic acid, (E)-3-(3-fluorophenyl)-2-(4-chlorophenyl)-2-propenoic acid (Fig. 1) and its organotin compounds.

2. Results and discussion

Reaction of R_2SnCl_2 and R_3SnCl with the silver salt of (E)-3-(3-fluorophenyl)-2-(4-chlorophenyl)-2-propenoic acid in 1:2 and 1:1 molar ratio, respectively, led to the formation of complexes according to Eqs. (1) and (2).
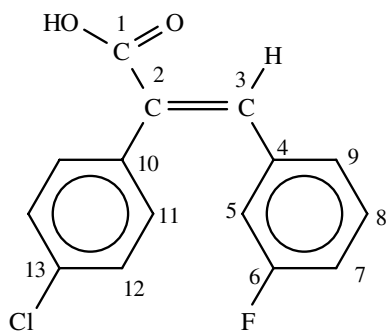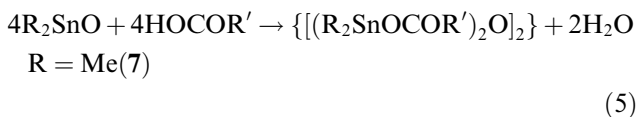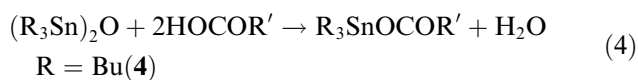

Fig. 1. Numbering scheme and structure of the (E)-3-(3-fluorophenyl)-2-(3-chlorophenyl)-2-propenoic acid (**HL**).

Reactions of n-Bu$_2$SnO, (n-Bu$_3$Sn)$_2$O and n-Oct$_2$SnO with ligand acid (1:2 molar ratio) in boiling toluene afforded the compounds **3**, **4** and **9**, respectively, with azeotropic removal of water (Eqs. (3) and (4)). The compound **7** was synthesized according to the reported method by refluxing the Me$_2$SnO with ligand acid in toluene (1:1 molar ratio) as shown in Eq. (5) [11].

$$R_2SnCl_2 + 2AgOCOR' \rightarrow R_2Sn(OCOR')_2 + 2AgCl$$
$$R = Me(\mathbf{1}), Bz(\mathbf{6}), Et(\mathbf{8})$$

(1)

$$R_3SnCl + AgOCOR' \rightarrow R_3SnOCOR' + AgCl$$
$$R = Me(\mathbf{2}), Ph(\mathbf{5})$$

(2)

$$R_2SnO + 2HOCOR' \rightarrow R_2Sn(OCOR')_2 + H_2O$$
$$R = Bu(\mathbf{3}), Oct(\mathbf{9})$$

(3)

$$(R_3Sn)_2O + 2HOCOR' \rightarrow R_3SnOCOR' + H_2O$$
$$R = Bu(\mathbf{4})$$

(4)

$$4R_2SnO + 4HOCOR' \rightarrow \{[(R_2SnOCOR')_2O]_2\} + 2H_2O$$
$$R = Me(\mathbf{7})$$

(5)

where $R' = (4\text{-}ClC_6H_4)C = CH(3\text{-}FC_6H_4)$.

$R = \overset{\alpha}{C}H_3, \quad R = \overset{\alpha}{C}H_2\overset{\beta}{C}H_3$

$R = \overset{\alpha}{C}H_2\overset{\beta}{C}H_2\overset{\gamma}{C}H_2\overset{\delta}{C}H_3$

$R = \overset{\alpha}{C}H_2\overset{\beta}{C}H_2\overset{\gamma}{C}H_2\overset{\delta}{C}H_2\overset{\alpha^*}{C}H_2\overset{\beta^*}{C}H_2\overset{\gamma^*}{C}H_2\overset{\delta^*}{C}H_3$
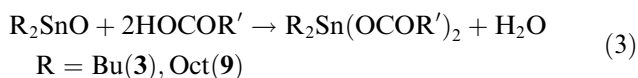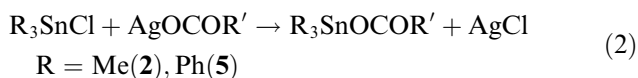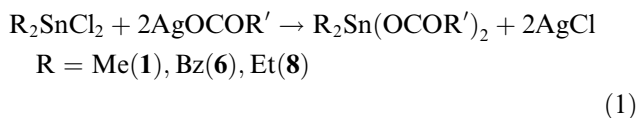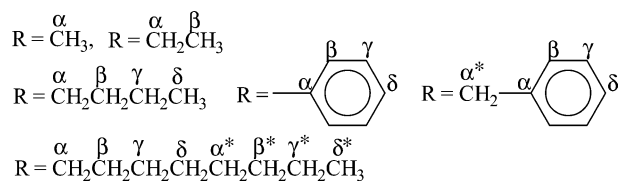
All the synthesized compounds are stable, soluble in common organic solvents and their physical data are collected in Table 1.

2.1. Spectroscopic characterization

Structural characterizations are based on the IR spectroscopy, multinuclear NMR (^{1}H, ^{13}C, ^{119}Sn) and X-ray single crystal analysis of the compound **5**.

2.2. Infrared spectroscopy

Vibrational data of the synthesized compounds are collected in Table 2 and the coordination mode of the ligand acid towards the di- and tri-organotin(IV) moieties can be deduced by comparing the infrared spectra of free acid, its salt and organotin compound. Diagnostically important IR bands are $v(OCO)_{asym}$, $v(OCO)_{sym}$,

v(Sn–C) and v(Sn–O). The magnitude of Δv(OCO) is in the range of 186–206 cm^{-1} except for compound **5**, indicating a bidentate nature of the carboxylate towards the Sn atom [12].

Thus according to the earlier reports featuring the same results and crystallographic data, it is most likely that in diorganotin compounds **1**, **3**, **6**, **8** and **9**, the tin atom approaches six coordination based on the skew-trapezoidal planar geometry [13] and the carboxylate group acts as an asymmetric bidentate ligand. This bidentate nature of the carboxylate ligand also suggests five-coordinated tin atoms in the triorganotin compounds **2** and **4**. In accordance to earlier reports, triorganotin carboxylates with bridging ligands lead to *trans*-R$_3$SnO$_2$ geometry for tin (Scheme 1).

Thus on the basis of similar results reported earlier, we propose trigonal bipyramidal linear polymer structures for compounds **2** and **4** are proposed [14]. The Δv(OCO) value for compound **5** is 243 cm^{-1}, which suggests a monodentate bonding mode of the carboxylate group to organotin(IV) moiety. Fortunately, X-ray crystal structure data are available to support the IR data for compound **5**. The discussion on X-ray crystal structure of compound **5** will be described in the proceeding section. IR spectrum of the compound **7** (dimeric dicarboxylatotetraorganodistannoxane) is almost similar to the diorganotin compounds except for a very sharp band at 686 cm^{-1}, characteristics

Table 1
Physical data of the synthesized organotin(IV) derivatives of (*E*)-3-(3-fluorophenyl)-2-(4-chlorophenyl)-2-propenoic acid

Compound no.	Compound (Formula Weight)	M.P. (°C)	Yield (%)	%C Calc. (found)	%H Calc. (found)
1	Me$_2$SnL$_2$ C$_{32}$H$_{24}$Cl$_2$F$_2$O$_4$Sn (700)	207–210	82.3	54.86 (54.77)	3.43 (3.49)
2	Me$_3$SnL C$_{18}$H$_{18}$ClFO$_2$Sn (439.5)	128–130	90.5	49.15 (49.21)	4.10 (4.08)
3	*n*-Bu$_2$SnL$_2$ C$_{38}$H$_{36}$Cl$_2$F$_2$O$_4$Sn (784)	123–125	78.9	58.16 (58.08)	4.59 (4.61)
4	*n*-Bu$_3$SnL C$_{27}$H$_{36}$ClFO$_2$Sn (565.5)	Liquid	80.0	57.29 (57.31)	6.37 (6.34)
5	Ph$_3$SnL C$_{33}$H$_{24}$ClFO$_2$Sn (625.5)	142–144	75.5	63.31 (63.38)	3.84 (3.90)
6	Bz$_2$SnL$_2$ C$_{44}$H$_{32}$Cl$_2$F$_2$O$_4$Sn (852)	84–86	65.7	61.97 (61.89)	3.76 (3.73)
7	[(Me$_2$SnL)$_2$O]$_2$ C$_{68}$H$_{60}$Cl$_4$F$_4$O$_{10}$Sn$_4$ (1730)	196–198	73.6	47.17 (47.19)	3.47 (3.50)
8	Et$_2$SnL$_2$ C$_{34}$H$_{28}$Cl$_2$F$_2$O$_4$Sn (728)	178–180	80.6	56.04 (56.11)	3.85 (3.81)
9	*n*-Oct$_2$SnL$_2$ C$_{46}$H$_{52}$Cl$_2$F$_2$O$_4$Sn (896)	59–61	70.4	61.61 (61.56)	5.80 (5.77)

Table 2
Infrared data (cm^{-1}) of organotin(IV) derivatives of (*E*)-3-(3-fluorophenyl)-2-(4-chlorophenyl)-2-propenoic acid

Compound no.	v(COO)		Δv	v(Sn–C)	v(Sn–O)	v(Sn–O–Sn)
	Asym.	Sym.				
1	1580	1392	188	546	491	–
2	1571	1373	198	554	489	–
3	1584	1391	193	542	492	
4	1581	1375	206	552	485	
5	1630	1387	243	–	490	–
6	1578	1392	186	571	449	
7	1583	1390	193	558	493	686
8	1579	1392	187	543	490	–
9	1578	1391	187	548	490	–
HL (Acid)	1676	1285	391	–	–	–
AgL	1567	1356	211	–	–	–
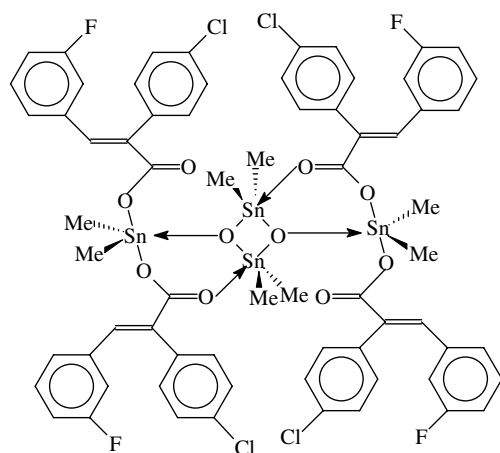
Scheme 2. The structure of {[Me₂SnOCOC(4-ClC₆H₄) = CH(3-FC₆H₄)]₂O}₂.

for $\overset{\frown}{Sn}$ —O —$\overset{\frown}{Sn}$ —O ring in this compound [15] (Scheme 2).

2.3. X-ray structure of 5

The molecular structure of Ph₃SnOCOC(4-ClC₆H₄) = CH(3-FC₆H₄), **5** is shown in Fig. 2. Experimental data pertinent to structure refinement and selected interatomic parameters for compound **5** are listed in Tables 3 and 4, respectively.

The structure is in agreement with the results obtained from infrared spectroscopy and the lattice is comprised of discrete molecules of the compound. The Sn atom exists in a distorted tetrahedral geometry defined by three *ipso*-C atoms of the phenyl groups and O1 atom [Sn1–O1 = 2.0557(14) Å] of the (E)-3-(3-fluorophenyl)-2-(4-chloropheny)-2-propenoate. The major distortion

Table 3
Crystal data and structure refinement for compound **5**

Empirical formula	C₃₃H₂₄ClFO₂Sn
Formula weight	625.66
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P$\bar{1}$
Unit cell dimensions	
a (Å)	10.8271(11)
b (Å)	11.4222(12)
c (Å)	13.6002(16)
α (°)	68.915(8)
β (°)	76.275(6)
γ (°)	61.919(7)
Volume (Å³)	1379.9(3)
Z	2
$D_{(calc)}$ (Mg/m³)	1.506
Absorption coefficient (mm⁻¹)	1.058
F(000)	628
Crystal size (mm³)	0.12 × 0.10 × 0.09
θ Range for data collection (°)	1.6–30.4
Index ranges	−15 ⩽ h ⩽ 15, −16 ⩽ k ⩽ 15, −19 ⩽ l ⩽ 19
Reflections collected	15,288
Independent reflections	8107 [$R_{(int)}$ = 0.038]
Completeness to θ = 30.4°	96.8%
Absorption correction	Multi-scan method
Maximum and minimum transmission	0.911 and 0.884
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	8107/0/353
Goodness-of-fit on F^2	1.03
Final R indices [I > 2σ(I)]	R_1 = 0.035, wR_2 = 0.068
R indices (all data)	R_1 = 0.054, wR_2 = 0.074
Largest diff. peak and hole (e Å⁻³)	0.88 and −0.52

from the ideal tetrahedral geometry is found in the O1–Sn1–C1 angle of 96.54(7)°. The relatively close interaction between O2 and Sn1 [Sn1···O2 = 2.8309(15) Å],
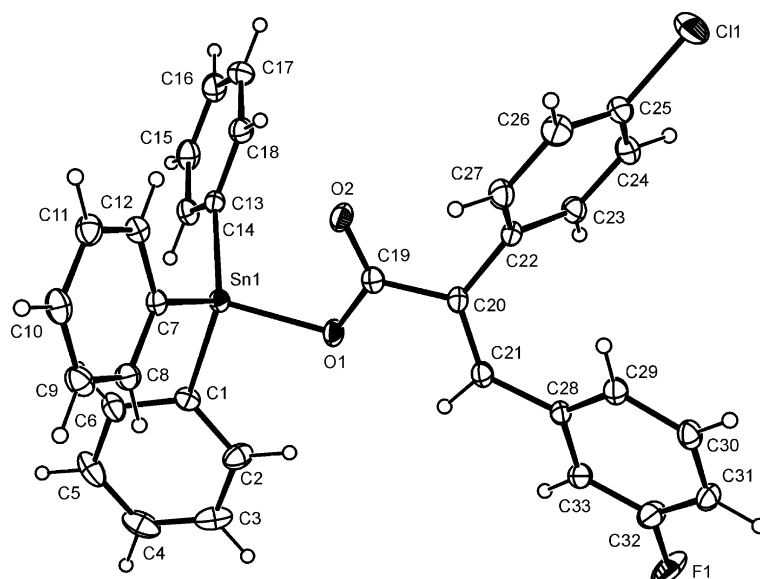

Fig. 2. ORTEP drawing of the X-ray structure of compound **5**.

Table 4
Selected geometric parameters (Å, °) for compound **5**

Sn(1)–O(1)	2.0557(14)	O(2)–C(19)	1.229(2)
Sn(1)–C(7)	2.118(2)	C(19)–C(20)	1.488(3)
Sn(1)–C(13)	2.126(2)	C(20)–C(21)	1.347(3)
Sn(1)–C(1)	2.127(2)	C(20)–C(22)	1.494(3)
O(1)–C(19)	1.313(2)	C(21)–C(28)	1.475(3)
O(1)–Sn(1)–C(7)	108.91(7)	C(6)–C(1)–C(2)	117.9(2)
O(1)–Sn(1)–C(13)	110.10(7)	C(6)–C(1)–Sn(1)	119.60(16)
C(7)–Sn(1)–C(13)	119.06(8)	C(2)–C(1)–Sn(1)	122.41(16)
O(1)–Sn(1)–C(1)	96.54(7)	C(12)–C(7)–Sn(1)	121.79(15)
C(7)–Sn(1)–C(1)	108.23(8)	C(8)–C(7)–Sn(1)	119.74(15)
C(13)–Sn(1)–C(1)	111.63(8)	C(18)–C(13)–Sn(1)	123.49(16)
C(19)–O(1)–Sn(1)	111.14(12)	C(14)–C(13)–Sn(1)	117.88(15)
O(2)–C(19)–C(20)–C(21)	168.1(2)	O(1)–C(19)–C(20)–C(22)	168.41(19)
O(1)–C(19)–C(20)–C(21)	−10.4(3)	C(19)–C(20)–C(21)–C(28)	−173.2(2)
O(2)–C(19)–C(20)–C(22)	−13.0(3)		

does not disrupt the O1–Sn1–C7 and O1–Sn1–C13 angles significantly, which are 108.91(7)° and 110.10(7)°, respectively. However, it is noteworthy that the C7–Sn1–C13 angle of 119.06(8)° is the next major distortion from the ideal geometry. The monodentate mode of coordination of the (*E*)-3-(3-fluorophenyl)-2-(4-chloropheny)-2-propenoate is reflected in the disparate O1–C19 and O2–C19 bond distances of 1.313(2) and 1.229(2) Å, respectively, with the longer separation being associated with the stronger Sn1–O1 interaction. The structural motif presented here for $C_{33}H_{24}ClFO_2Sn$ is one of the two major motifs found for compounds of the general formula R_3SnO_2CR' [16]. These bond distances and angles are in agreement with the corresponding values found for similar Sn complexes contained in the Cambridge Structural Database [4,17].

2.4. Multinuclear (^1H, ^{13}C, ^{119}Sn) NMR

Multinuclear NMR spectra (^1H, ^{13}C and ^{119}Sn) for new compounds and free acid have been recorded in $CDCl_3$ solution and reported in Tables 5 and 6. The olefinic proton in acid and its organotin derivatives appear in the range 7.13–7.31 ppm as a singlet. The signals of different aromatic protons in the acid have been assigned with their distinct multiplicity pattern and *J* values and consistent with expectation. A set of similar pattern of the signals has been observed for the investigated compounds. The methyl protons in dimethyltin **1** and trimethyltin **2** derivatives appear as sharp singlet with $^2J[^{119}Sn, {}^1H]$ coupling of 79.6 and 58.4 Hz, respectively. The *n*-butyl protons in compounds **3** and **4** show a complex pattern due to $CH_2–CH_2–CH_2–$ skeleton in the range of 1.25–1.75 ppm and clear triplet due to the terminal methyl groups at 0.96 and 0.94 ppm, respectively. A complex pattern for aromatic protons in case of triphenyltin **5** and dibenzyltin **6** have also been observed in expected region.

The methylene protons of benzyl group in **6** resonate at 2.25 ppm as singlet. The protons of $SnCH_2CH_3$ group in **8** appear at 1.05 and 0.68 ppm with distinct quartet and triplet, respectively. The methylene protons $(CH_2)_7$ moiety of compound **9** exhibit a somewhat different behaviour compared with *n*-butyl group of the respective compounds. These protons give broad signals in the range 1.75–1.10 ppm compatible with the values calculated by incremental method [18]. However, the terminal CH_3 protons appear as a triplet at 0.57–0.68 ppm with $^3J[^1H, {}^1H]$ coupling of 6.6 Hz.

The ^{13}C NMR spectral data for ligand acid is enlisted in Table 6 along with its organotin derivatives. The assignment of ^{13}C signal for –COO and olefinic carbon atoms are straightforward and are assigned by comparison with related other organic analogues [18]. The position of carbon atoms in fluorophenyl group are easily assigned with the help of $^nJ(^{19}F, {}^{13}C)$ couplings, where $n = 1,2,3,4$. While the position of carbon atoms in chlorophenyl moiety are resolved by comparing with analogue, (*E*)-3-(4-chlorophenyl)-2-phenyl-2-propenoic acid [18,19]. The $^nJ(^{19}F, {}^{13}C)$ coupling constants are listed in Table 6 and are comparable to those reported earlier. The reported range of the $^nJ(^{19}F, {}^{13}C)$ couplings, where $n = 1,2,3,4$ are 230–265, 15–25, 7–12, 3 Hz [20]. The values we observed are 245.8–246.4, 21–22, 7.4–8.7 and 2.2–2.5 Hz for $^nJ(^{19}F, {}^{13}C)$, where $n = 1,2,3,4$, respectively. The complete assignments of signals of alkyl/aryl carbons attach to tin are based on $^nJ[^{119}Sn, {}^{13}C]$ coupling and comparison with related analogues as model compounds [15,20]. The coupling constants $^1J[^{119}Sn, {}^{13}C]$ are important indicators for structural evaluation of organotin carboxylates. Holecek and coworkers [21,22] have shown that for four-coordinated trialkyltin and triphenyltin compounds the coupling constants, $^1J[^{119}Sn, {}^{13}C]$ occur in the range of 325–400 and 550–670 Hz, respectively, while five-coordinated tin compounds exhibit couplings in the range of 440–540 and 750–850 Hz, respectively.

Table 5
^{1}H NMR data of organotin(IV) derivatives of (*E*)-3-(3-fluorophenyl)-2-(4-chlorophenyl)-2-propenoic acid[a,b,c]

Proton no.	Ligand	1	2	3	4	5	6	7	8	9
3	7.25 s	7.30 s	7.14 s	7.30 s	7.13 s	7.26 s	7.25 s	7.30 s	7.31 s	7.30 s
5	6.22 d (7.7)	6.23 d (7.7)	6.18 d (7.8)	6.24 d (7.7)	6.19 d (8.0)	6.18 d (7.9)	6.10 d (7.5)	6.23 d (7.7)	6.24 d (7.9)	6.23 d (7.7)
7	6.09 dd (10,8)	6.10 dd (9.9,8)	6.06 dd (10,8)	6.11 dd (10,8)	6.07 dd (10,8)	6.07 dd (10,8)	5.97 dd (10,8)	6.10 dd (9.9,8)	6.11 dd (10.3,8)	6.10 dd (9.9,8)
8	6.32 dd (8.4,8)	6.30 dd (8.3,8)	6.24 dd (8.3,8)	6.30 dd (8.3,8)	6.23 dd (8.3,8)	6.26 dd (8.2,8)	6.27 dd (8.2,8)	6.30 dd (8.3,8)	6.29 dd (8.2,6)	6.30 dd (8.3,8)
9	6.28 dd (8.6,2.6)	6.30 dd (8.3,2.5)	6.24 dd (8.6,2.5)	6.36 dd (8.4,2.6)	6.30 dd (8.5,2.6)	6.30 dd (8.2,2.4)	6.30 dd (8.4,2.5)	6.35 dd (8.3,2.2)	6.31 dd (8.4,2.5)	6.34 dd (8.3,2.2)
11	6.71 d (8.6)	6.70 d (8.3)	6.64 d (8.3)	6.70 d (8.5)	6.64 d (8.4)	6.66 d (8.3)	6.57 d (7.9)	6.70 d (8.3)	6.56 d (7.9)	6.70 d (8.3)
12	6.51 d (8.6)	6.52 d (8.4)	6.49 d (8.4)	6.52 d (8.5)	6.49 d (8.4)	6.50 d (8.2)	6.48 d (8.5)	6.52 d (8.4)	6.49 d (8.5)	6.52 d (8.4)

[a] Compound **1**: Sn–CH$_3$, 0.42 s ^2J[79.6]. Compound **2**: Sn–CH$_3$, −0.06 s ^2J[55.9, 58.4]. Compound **3**: Sn–CH$_2$CH$_2$CH$_2$CH$_3$, 0.7–1.2 m, 0.25 t (7.3). Compound **4**: Sn–CH$_2$CH$_2$CH$_2$CH$_3$, 0.60–0.96 m, 0.25 t (7.3). Compound **5**: Sn–C$_6$H$_5$, 6.74–6.81 m, 7.07–7.10 m. Compound **6**: Sn–CH$_2$C$_6$H$_5$, 2.25 s, 6.65–6.78 m, 6.85–7.01 m. Compound **7**: Sn–CH$_3$, 0.03 s, 0.09 s. Compound **8**: Sn–CH$_2$CH$_3$, 1.05 q (8.2), 0.68 t, (7.9). Compound **9**: Sn–CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$, 1.75–1.10 m, 0.57–0.68 m, 0.17 t, (6.6).

[b] Chemical shifts (δ) in ppm. ^2J[$^{117/119}$Sn, ^{1}H]; ^2J[^{119}Sn, ^{1}H]; and ^3J(^{1}H, ^{1}H) in Hz are listed in square brackets and parenthesis, respectively. ^nJ(^{19}F–^{1}H) are given in italic. Multiplicity is given as: s, singlet; d, doublet; dd, doublet of doublet; q, quartet; t, triplet; m, multiplet.

Table 6
^{13}C and ^{119}Sn NMR data of organotin(IV) derivatives of (*E*)-3-(3-fluorophenyl)-2-(4-chlorophenyl)-2-propenoic acid[a,b,c]

Carbon no.	Ligand	1	2	3	4	5	6	7	8	9
1	172.62	176.69	171.93	176.51	171.72	172.89	174.10	176.69	176.68	176.47
2	131.62	131.98	133.64	132.28	133.5	133.11	133.47	131.98	132.07	132.27
3	141.62	141.05	138.55	140.65	138.05	140.0	140.77	141.05	140.78	140.63
4	136.0 d (7.9)	136.4, d (7.6)	137.14 d (7.9)	136.52 d (8.1)	137.28 d (7.4)	137.22	136.33 d (7.2)	136.38 d (7.6)	136.45 d (8.3)	136.52, d (7.4)
5	116.7 d (21.6)	116.37 d (21.7)	115.6 d (21.3)	116.26 d (21.4)	115.44 d (21.0)	115.85 d (21.3)	116.34 d (21.4)	116.37 d (21.7)	116.31 d (21.2)	116.24 d (21.6)
6	162.35 d (246.4)	162.36 d (246.1)	162.35 d (245.8)	162.37 d (246.3)	162.36 d (245.8)	162.35 d (246.0)	162.31 d (246.3)	162.36 d (246.1)	162.27 d (246.2)	162.26 d (246.2)
7	117.05 d (22.8)	116.85 d (22.9)	116.65 d (22.3)	116.88 d (22.7)	116.61 d (22.0)	116.74 d (22.3)	116.91 d (22.0)	116.85 d (22.9)	116.88 d (22.5)	116.85 d (22.9)
8	129.93 d (8.2)	129.86 d (7.9)	129.66 d (8.2)	129.84 d (8.7)	129.60 d (8.3)	129.72 d (8.3)	129.82 d (7.8)	129.86 d (7.9)	129.85 d (8.1)	129.83 d (8.1)
9	126.57	126.36	126.09 d (2.5)	126.38 d (2.2)	126.07 d (2.4)	126.18 d (2.4)	126.4	126.36	126.39 d (2.0)	126.36 d (2.4)
10	132.95	133.59	134.17	133.85	134.63	133.81	133.94	133.59	133.8	133.84
11	129.10	129.02	128.72	129.04	128.62	128.93	128.79	129.02	129.06	129.02
12	131.15	131.12	131.21	131.09	131.15	131.30	131.23	131.12	131.08	131.09
13	134.44	134.24	134.77	134.16	135.14	134.45	134.48	134.24	134.19	134.16

[a] Compound **1**: Sn–CH$_3$, (C-α) 4.38. δ ^{119}Sn: −127.3. Compound **2**: Sn–CH$_3$, (C-α) −2.18 ^1J[378.2,396.3]. δ ^{119}Sn: 142.0. Compound **3**: Sn–CH$_2$CH$_2$CH$_2$CH$_3$, (C-α) 25.42, (C-β) 26.70, (C-γ) 26.28, (C-δ) 13.61. δ ^{119}Sn: −155.8. Compound **4**: Sn–CH$_2$CH$_2$CH$_2$CH$_3$, (C-α) 16.56 ^1J[344,360], (C-β) 27.83 ^2J[21.0], (C-γ) 26.99 ^3J[63.0], (C-δ) 13.66. δ ^{119}Sn: 115.3. Compound **5**: Sn–C$_6$H$_5$, (C-α) 138.07 ^1J[639.4,661.5], (C-β) 136.91 ^2J[48.0], (C-γ) 130.22, (C-δ) 128.74. δ ^{119}Sn: −107.7. Compound **6**: Sn–CH$_2$C$_6$H$_5$, (C-α*) 29.69 ^1J[516.5], (C-α) 134.03, (C-β) 129.30, (C-γ) 128.08, (C-δ) 126.99. δ ^{119}Sn: Not measured. Compound **7**: Sn–CH$_3$, (C-α) 9.14, 7.34. δ ^{119}Sn: −177.7, −179.4. Compound **8**: Sn–CH$_2$CH$_3$, (C-α) 17.82, (C-β) 9.02. δ ^{119}Sn: −161.8. Compound **9**: Sn–CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$, (C-α) 25.68 ^1J[556,581], (C-β) 24.58 ^2J[37.0], (C-γ) 33.16 ^3J[94.6], (C-δ) 29.13, (C-α*) 29.07, (C-β*) 31.82, (C-γ*) 22.62, (C-δ*) 14.07. ^{119}Sn: −155.5.

[b] Chemical shifts (δ) in ppm. ^1J[$^{117/119}$Sn, ^{13}C]; ^nJ[^{119}Sn, ^{13}C] and ^nJ(^{19}F, ^{13}C) in Hz are listed in square brackets and parenthesis, respectively.

[c] Numbering is according to Fig. 1.

In present investigation all the triorganotin carboxylates exhibit $^1J[^{119}Sn, ^{13}C]$ coupling satellites in solution, characteristics of the tetrahedral compounds; the coupling constants being of the order of 396.3, 360 and 661.5 Hz in trimethyltin **2**, tri-*n*-butyltin **4** and triphenyltin **5** compounds, respectively. Thus bidentate nature of the ligand acid resulting in penta-coordinated compounds in solid state is therefore lost in solution to generate a monomeric four-coordinated tetrahedral structure for compounds **2** and **4**. In contrast triphenyltin(IV) derivative, **5** shows a tetrahedral geometry both in solid and solution states. Various literature methods have been applied to calculate the C–Sn–C bond angles in solution based on $^2J(^{119}Sn, ^1H)$ and $^1J(^{119}Sn, ^{13}C)$ coupling constants (Table 7) [23,24]. By the use of Lockhart and Holeček equations, the values obtained were 111.5°, 110.7° and 116.8°, respectively, for trimethyltin, tri-*n*-butyltin and triphenyltin(IV) derivatives. The geometrical data calculated are consistent with tetrahedral geometries for triorganotin(IV) compounds i.e., monomers in solution.

In diorganotin compounds, $^1J[^{119}Sn, ^{13}C]$ coupling satellites were observed only for compounds **6** and **9**, which suggest coordination number higher than 4 in comparisons with the reported values [25]. We emphasized therefore, on the ^{119}Sn NMR (Table 6, foot note) in order to deduce the coordination of tin atom in diorganotin compounds. Compounds **1**, **3**, **8** and **9** exhibit a single ^{119}Sn resonance signal at −127.3, −155.8, −161.8 and −155.5 ppm, respectively, that is characteristic of penta-coordinated tin atom as earlier reports manifested [19,25,26]. On the other hand triorganotin compounds give a single resonance peak in the range characteristic for the tetrahedral compounds. This confirms the four-coordination proposed from ^{13}C data and also supports the single crystal structure of compound **5**. For compound **7** two ^{119}Sn resonances were observed (−177.7 and −179.4 ppm) and assigned to the endocyclic and exocyclic tin atoms (Scheme 1). These values are in agreement with the literature values reported for similar distannoxanes [11,27].

2.5. Mass spectrometry

The conventional EI mass spectral data for ligand acid and its organotin derivatives are recorded and different fragmentation patterns have been proposed and are listed in the Scheme 3–5 along with *m/z* and % intensity. The molecular ion peak M$^{+\cdot}$ for ligand acid appeared as base peak along with M + 2 with 33% intensity due to isotopic ^{37}Cl. Loss of different groups like H, Cl, F, COO, COOH result in different peaks of respective *m/z*, which on further loss gave a peak at *m/z* 177 (10) for the positive ion $C_6H_4CCHC_6H_4$. The further elimination of CCH group produced fragment ion $[C_6H_4–C_6H_4]^+$ at *m/z* 152 (25). In addition *m/z* at 77 and 75 also observed for $[C_6H_5]^+$ and $[C_6H_3]^+$ fragment ions, respectively. In mass spectral data of tri- and di-organotin(IV) derivatives, each fragment ion occurs in a group of peaks as a result of tin isotopes. For simplicity the mass spectral fragmentation data reported here is related to the principal isotope ^{120}Sn [28]. The molecular ion peaks, M$^{+\cdot}$, have been exceptionally observed in all compounds, even in low relative abundance. In triorganotin compounds three primary fragmentation patterns are proposed, based on observed *m/z* in their spectra. Elimination of different groups like COOR′ and R, gave $[Sn]^+$ as end product in one of the pathways. The other two pathways after primary elimination of $[R]^+$ and $[R_3Sn]^+$ groups and then elimination of COO and successive R (in one of the pathway) results in the formation of $[R′]^+$, which shows similar pattern for the further elimination of different groups. A somewhat different scheme of mass fragementaion pattern has been suggested for the diorganotin compounds but these pathways end up in similar fashion as suggested for the triorganotin compounds. In addition, the following ions are also observed with reasonable intensities in the mass spectra of all organotin(IV) derivatives: $[C_8H_{17}]^+$, $[C_6H_5CH_2]^+$, $[C_6H_5]^+$, $[C_4H_9]^+$ and $[C_3H_7]^+$.

3. Biological activity

3.1. Antibacterial activity

Almost all of the synthesized compounds were subjected to screening test for their antibacterial activity, using the agar well diffusion method [29] and data are listed in Table 8. It is concluded that organotin(IV) derivatives of ligand acid show marginally high activity than the acid itself but considerably lower than the reference drug.

Table 7
(C–Sn–C) angles (°) based on NMR parameters of selected organotin(IV) derivatives of (E)-3-(3-fluorophenyl)-2-(4-chlorophenyl)-2-propenoic acid

Compound no.	Compound	$^1J[^{119}Sn, ^{13}C]$ (Hz)	$^2J[^{119}Sn, ^1H]$ (Hz)	θ (°)	
				^1J	^2J
1	Me$_2$SnL$_2$	–	79.6	–	130.3
2	Me$_3$SnL	396.3	58.4	111.5	111.2
4	*n*-Bu$_3$SnL	360	–	110.7	–
5	Ph$_3$SnL	661.5	–	116.8	–

$[C_6H_3]^+$ 75 (8)

↑ $-C_6H_5$

$[C_6H_4 \!-\! C_6H_4]^+$
152 (25) ↑ $-CCH$

↑ $-CCH$ ↑ $-CCH$

$[C_6H_4)CCH(C_6H_4)]^+$ $[(C_6H_4)CCH(C_6H_4)]^+$ $[(C_6H_4)CCH(C_6H_4)]^+$

177 (10) ↑ $-F$ 177 (10) ↑ $-F$ 177 (10) ↑ $-Cl$

$[(C_6H_4)CCH(3\text{-}FC_6H_4)]^+$ $[(C_6H_4)CCH(3\text{-}FC_6H_4)]^+$ $[(4\text{-}ClC_6H_4)CCH(C_6H_4)]^+$

196 (62) ↑ $-Cl$ 196 (62) ↑ $-CO_2$ 212 (2) ↑ $-CO_2$

$[(4\text{-}ClC_6H_4)CCH(3\text{-}FC_6H_4)]^+$ $[OOC(C_6H_4)CCH(3\text{-}FC_6H_4)]^+$ $[OOC(4\text{-}ClC_6H_4)CCH(C_6H_4)]^+$

231 (25) ↑ $-CO_2$ 240 (1) ↑ $-H$ 256 (1) ↑ $-H$

$[OOC(4\text{-}ClC_6H_4)CCH(3\text{-}FC_6H_4)]^+$ $[HOOC(C_6H_4)CCH(3\text{-}FC_6H_4)]^+$ $[HOOC(4\text{-}ClC_6H_4)CCH(C_6H_4)]^+$

275 (2)   241 (22)   257 (3)

↖ $-H$ ↑ $-Cl$ ↗ $-F$

$[HOOC(4\text{-}ClC_6H_4)CCH(3\text{-}FC_6H_4)]^{+\bullet}$

276 (100)

↙ $-CO_2$ $-CO_2H$ ↘

$[H(4\text{-}ClC_6H_4)CCH(3\text{-}FC_6H_4)]^+$ → $[(4\text{-}ClC_6H_4)CCH(3\text{-}FC_6H_4)]^+$

232 (18)   231 (25)

↓ $-Cl$ ↓ $-Cl$

$[H(C_6H_4)CCH(3\text{-}FC_6H_4)]^+$ $[(C_6H_4)CCH(3\text{-}FC_6H_4)]^+$

197 (30)   196 (62)

↘ $-HF$ ↙ $-F$

$[(C_6H_4)CCH(C_6H_4)]^+$

177 (10)

↓ $-CCH$

$[C_6H_4 \!-\! C_6H_4]^+$

152 (25) ↓ $-C_6H_5$

$[C_6H_3]^+$

75 (8)

Scheme 3. Mass fragmentation pattern of (*E*)-3-(3-fluorophenyl)-2-(4-chlorophenyl)-2-propenoic acid.

The results further demonstrated that diorgano-tin(IV) compounds show better activity against various bacteria than triorganotin(IV) derivatives.

3.2. Antifungal activity

The selected synthesized compounds were tested for antifungal activity against various pathogens by using the tube diffusion test [30] and the data collected are listed in Table 9. Generally all of the selected derivatives including the parent ligand show markedly lower anti-fungal activity than the standard drugs (Table 9). It

has been reported that within a given series the triorg-anotin(IV) derivatives are more active various against fungi. Although our screening tests are not very pronouncing but still are quite consistent with the earlier reports [31]. The importance of the organotin moiety present is seen when one considers that the free acid has less biocidal activity.

3.3. Cytotoxicity

These compounds were also evaluated for cytotoxicity data, using brine-shrimp (*Artemia salina*) bioassay

$[R_3SnOCOR']^+$ ·
(**2**) R = Me, 440 (4)
(**4**) R = Bu, 566 (5)
(**5**) R = Ph, 626 (8)

−R_3Sn

$[OCOR']^+$
(**2**) 275 (2)
(**4**) 275 (2)
(**5**) 275 (6)

−CO_2

$[R' = (4\text{-}ClC_6H_4)CCH(3\text{-}FC_6H_4)]^+$
(**2**) 231 (35)
(**4**) 231 (15)
(**5**) 231 (70)

−Cl

$[(C_6H_4)CCH(3\text{-}FC_6H_4)]^+$
(**2**) 196 (45)
(**4**) 196 (20)
(**5**) 196 (30)

−F
−C=CH

$[C_6H_4\!-\!C_6H_4]^+$
(**2**) 152 (5)
(**4**) 152 (10)
(**5**) 152 (15)

−C_6H_4

$[C_6H_4]^+$
(**2**) 76 (3)
(**4**) 76 (3)
(**5**) 76 (3)

−OCOR'

$[R_3Sn]^+$
(**2**) R = Me, 165 (30)
(**4**) R = Bu, 291 (18)
(**5**) R = Ph, 351 (50)

−R

$[R_2Sn]^+$
(**2**) R = Me, 150 (6)
(**4**) R = Bu, 234 (20)
(**5**) R = Ph, 274 (8)

−R

$[RSn]^+$
(**2**) R = Me, 135 (7)
(**4**) R = Bu, 177 (5)
(**5**) R = Ph, 197 (25)

−R

$[Sn]^+$
(**2**) 120 (4)
(**4**) 120 (5)
(**5**) 120 (8)

−R

$[R_2SnOCOR']^+$
(**2**) R = Me, 425 (100)
(**4**) R = Bu, 509 (100)
(**5**) R = Ph, 549 (100)

−CO_2

$[R_2SnR']^+$
(**2**) R = Me, 381 (30)
(**4**) R = Bu, 465 (2)
(**5**) R = Ph, 505 (10)

−R

$[RSnR']^+$
(**2**) R = Me, 366 (1)
(**4**) R = Bu, 408 (3)
(**5**) R = Ph, 428 (2)

−R

$[SnR']^+$
(**2**) 351 (5)
(**4**) 351 (10)
(**5**) 351 (50)

−Sn

−Cl

$[R']^+$
(**2**) 231 (35)
(**4**) 231 (15)
(**5**) 231 (70)

Scheme 4. Mass fragmentation pattern of triorganotin compounds.

lethality method [32] and results are summarized in Table 10, which substantiate that compounds **1**–**4** are non-toxic. However, compounds **5**, **6**, **8** and **9**, including ligand acid itself, showed high LD_{50} values in the range 206.1789–260.1139 µg/mL and exhibited low toxicity.
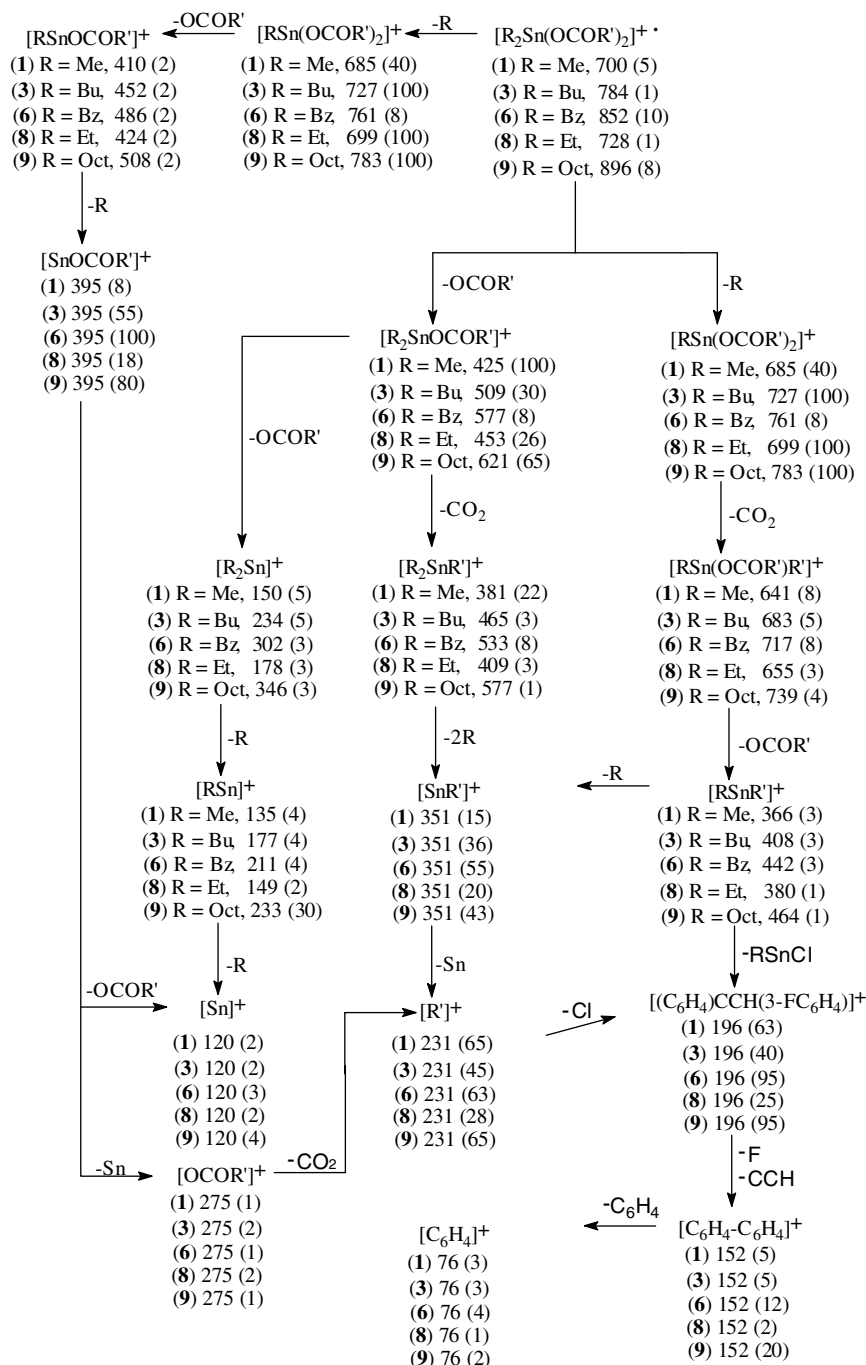
4. Conclusions

Organotin esters of (*E*)-3-(3-fluorophenyl)-2-(4-chlorophenyl)-2-propenoic acid are prepared successfully and characterized by the spectroscopic techniques. The ligand acts as bidentate as suggested by the IR analysis except for compound **5**, which in both solid and solution state shows the tetrahedral geometry around tin atom. The exhibition of charac-teristic IR bands and two signals of same intensity in ^{119}Sn NMR confirms compound **7** as dimeric dica-rboxylatotetraorganodistannoxane. Multinuclear NMR studies reveal the characteristic geometry in non-coor-dinating solvent for both di- and tri-organotin com-pounds. The selected synthesized compounds show remarkable cytotoxicity, bactericidal and fungicidal activities.

5. Experimental

All the di- and tri-organotin chlorides were procured from Aldrich or Fluka while dibenzyltin dichloride was prepared by the reported method [33]. The ligand (*E*)-3-(3-fluorophenyl)-2-(4-chlorophenyl)-2-propenoic   acid

[RSnOCOR']+ ←—-OCOR'— [RSn(OCOR')$_2$]+ ←—-R— [R$_2$Sn(OCOR')$_2$]+ •

[RSnOCOR']+	[RSn(OCOR')$_2$]+	[R$_2$Sn(OCOR')$_2$]+ •
(**1**) R = Me, 410 (2)	(**1**) R = Me, 685 (40)	(**1**) R = Me, 700 (5)
(**3**) R = Bu, 452 (2)	(**3**) R = Bu, 727 (100)	(**3**) R = Bu, 784 (1)
(**6**) R = Bz, 486 (2)	(**6**) R = Bz, 761 (8)	(**6**) R = Bz, 852 (10)
(**8**) R = Et, 424 (2)	(**8**) R = Et, 699 (100)	(**8**) R = Et, 728 (1)
(**9**) R = Oct, 508 (2)	(**9**) R = Oct, 783 (100)	(**9**) R = Oct, 896 (8)

-R

[SnOCOR']+
(**1**) 395 (8)
(**3**) 395 (55)
(**6**) 395 (100)
(**8**) 395 (18)
(**9**) 395 (80)

-OCOR' | -R

[R$_2$SnOCOR']+
(**1**) R = Me, 425 (100)
(**3**) R = Bu, 509 (30)
(**6**) R = Bz, 577 (8)
(**8**) R = Et, 453 (26)
(**9**) R = Oct, 621 (65)

[RSn(OCOR')$_2$]+
(**1**) R = Me, 685 (40)
(**3**) R = Bu, 727 (100)
(**6**) R = Bz, 761 (8)
(**8**) R = Et, 699 (100)
(**9**) R = Oct, 783 (100)

-OCOR'

[R$_2$Sn]+
(**1**) R = Me, 150 (5)
(**3**) R = Bu, 234 (5)
(**6**) R = Bz, 302 (3)
(**8**) R = Et, 178 (3)
(**9**) R = Oct, 346 (3)

-CO$_2$

[R$_2$SnR']+
(**1**) R = Me, 381 (22)
(**3**) R = Bu, 465 (3)
(**6**) R = Bz, 533 (8)
(**8**) R = Et, 409 (3)
(**9**) R = Oct, 577 (1)

-CO$_2$

[RSn(OCOR')R']+
(**1**) R = Me, 641 (8)
(**3**) R = Bu, 683 (5)
(**6**) R = Bz, 717 (8)
(**8**) R = Et, 655 (3)
(**9**) R = Oct, 739 (4)

-R

[RSn]+
(**1**) R = Me, 135 (4)
(**3**) R = Bu, 177 (4)
(**6**) R = Bz, 211 (4)
(**8**) R = Et, 149 (2)
(**9**) R = Oct, 233 (30)

-2R

[SnR']+
(**1**) 351 (15)
(**3**) 351 (36)
(**6**) 351 (55)
(**8**) 351 (20)
(**9**) 351 (43)

-OCOR'

[RSnR']+
(**1**) R = Me, 366 (3)
(**3**) R = Bu, 408 (3)
(**6**) R = Bz, 442 (3)
(**8**) R = Et, 380 (1)
(**9**) R = Oct, 464 (1)

←—-R—

-R

-OCOR' →

[Sn]+
(**1**) 120 (2)
(**3**) 120 (2)
(**6**) 120 (3)
(**8**) 120 (2)
(**9**) 120 (4)

-CO$_2$ →

[R']+
(**1**) 231 (65)
(**3**) 231 (45)
(**6**) 231 (63)
(**8**) 231 (28)
(**9**) 231 (65)

-Sn

-Cl →

-RSnCl

[(C$_6$H$_4$)CCH(3-FC$_6$H$_4$)]+
(**1**) 196 (63)
(**3**) 196 (40)
(**6**) 196 (95)
(**8**) 196 (25)
(**9**) 196 (95)

-F
-CCH

-Sn →

[OCOR']+
(**1**) 275 (1)
(**3**) 275 (2)
(**6**) 275 (1)
(**8**) 275 (2)
(**9**) 275 (1)

-C$_6$H$_4$ ←

[C$_6$H$_4$]+
(**1**) 76 (3)
(**3**) 76 (3)
(**6**) 76 (4)
(**8**) 76 (1)
(**9**) 76 (2)

[C$_6$H$_4$-C$_6$H$_4$]+
(**1**) 152 (5)
(**3**) 152 (5)
(**6**) 152 (12)
(**8**) 152 (2)
(**9**) 152 (20)

Scheme 5. Mass fragmentation pattern of diorganotin compounds.

was synthesized by the Perkin condensation method in the laboratory [34]. All the solvents were dried before use by the literature methods [35].

6. Instrumentation

Melting points were determined in capillary tubes using a MPD Mitamura Riken Kogyo (Japan) Electro thermal melting point apparatus and are uncorrected. Infrared absorption spectra were recorded as KBr pellets or neat liquid on a Bio-Rad *Excaliber* FT-IR, model FTS 3000 MX spectrometer (USA). ^{1}H, ^{13}C and ^{119}Sn NMR spectra were recorded on a Bruker AM 250 spectrometer (Germany), using CDCl$_3$ as an internal reference [δ ^{1}H(CDCl$_3$) = 7.25 and δ ^{13}C(CDCl$_3$) = 77.0]. ^{119}Sn NMR spectra were obtained with Me$_4$Sn as external reference [Ξ(Sn) = 37.290665]. Mass spectral data

Table 8
Antibacterial activity data of organotin(IV) derivatives of (E)-3-(3-fluorophenyl)-2-(4-chlorophenyl)-2-propenoic acid[a,b,c]

Name of bacterium	Zone of inhibition (mm)									Reference drug
	Ligand	1	2	3	4	5	6	8	9	
Escherichia coli	8	12	12	14	10	15	14	15	10	30
Bacillus subtilis	–	8	10	10	12	10	12	10	8	32
Shigella flexenari	–	–	–	8	8	10	10	10	10	41
Staphlococcus aureus	8	–	8	10	8	8	8	8	10	33
Pseudomonas aeruginosa	–	–	–	8	10	10	10	10	10	46
Salmonella typhi	10	8	8	8	8	10	10	10	10	29

–, Show no activity.
[a] In vitro, agar well diffusion method, conc. 3 mg/mL of DMSO.
[b] Reference drug, Imipenum.
[c] Clinical implication: *Escherichia coli*, infection of wounds, urinary tract and dysentery; *Bacillus subtilis*, food poisoning; *Shigella flexenari*, blood diarrhea with fever and severe prostration; *Staphlococcus aureus*, food poisoning, scaled skin syndrome, endrocarditis; *Pseudomonas aeruginosa*, infection of wounds, eyes, septicemia; *Salmonella typhi*, typhoid fever, localized infection.

Table 9
Antifungal activity data of organotin(IV) derivatives of (E)-3-(3-fluorophenyl)-2-(4-chlorophenyl)-2-propenoic acid[a,b,c]

Name of fungus	Percent inhibition							Standard drug	MIC (μg/mL)
	Ligand	1	2	3	4	5	8		
Trichophyton longifusus	–	12	–	20	20	10	–	Miconazole	70
Candida albicans	10	–	–	15	10	15	10	Miconazole	110.8
Aspergillus flavus	13	10	13	20	10	15	30	Amphotericin B	20
Microsporum canis	–	–	–	20	10	20	10	Miconazole	98.4
Fusarium solani	10	15	10	10	15	20	–	Miconazole	73.25
Candida glaberata	–	–	–	20	10	20	–	Miconazole	110.8

–, Show no activity.
[a] Concentration: 100 μg/mL of DMSO.
[b] MIC, minimum inhibitory concentration.
[c] Percent inhibition (standard drug) = 100.

Table 10
Cycotoxicity data of organotin(IV) derivatives of (E)-3-(3-fluoro- phenyl)-2-(4-chlorophenyl)-2-propenoic acid[a,b,c]

Compound	Ligand	1	2	3	4	5	6	8	9
LD$_{50}$	260.1139	–	–	–	–	207.1398	208.1498	207.1398	206.1789

[a] Against brine-shrimps, *Artemia salina* (in vitro).
[b] No cytotoxicity for compounds 1, 2, 3 and 4.
[c] Reference drug, Etoposide.

were measured on a MAT-8500 Finnigan 70 eV mass spectrometer (Germany). The *m/z* values were evaluated, assuming that H = 1, C = 12, Cl = 35, F = 19 and Sn = 120.

6.1. General procedure for synthesis

Methyl- 1, 2, phenyl- 5, benzyl- 6 and ethyltin(IV) 8, derivatives were prepared by heating at reflux temperature for 6–8 h, the corresponding diorganotin dichloride (10.64 mmol) or triorganotin chloride (5.32 mmol) with the silver salt of (E)-3-(3-fluorophenyl)-2-(4-chlorophenyl)-2-propenoic acid (5.32 mmol) in 1:2 and 1:1 molar ratio, respectively. The solvent used was dry chloroform (70 mL) contained in a 250 mL two-necked round bottom flask equipped with

water condenser and a magnet bar. It was placed overnight at room temperature, silver chloride (AgCl) formed was filtered off and solvent was evaporated under reduced pressure.

Di-*n*-butyl- 3, di-*n*-octyl- 9 and tri-*n*-butyltin(IV)- 4 carboxylates were synthesized by the condensation of (E)-3-(3-fluorophenyl)-2-(4-chlorophenyl)-2-propenoic acid (7.44 mmol) with the corresponding diorganotin oxides (14.87 mmol) and bis(tri-*n*-butyltin) oxide (7.44 mmol) in 2:1 molar ratio by heating at reflux temperature for 8–10 h in toluene (80 mL), using a Dean–Stark apparatus. All the products obtained were recrystallized from chloroform and *n*-hexane (4:1) mixture via slow evaporation at room temperature.

The dimeric stannoxanes 7 was prepared by refluxing the *n*-Bu₂SnO (7.74 mmol) for 8–10 h with (E)-3-(3-

fluorophenyl)-2-(4-chlorophenyl)-2-propenoic acid (7.74 mmol) in dry toluene (80 mL), using a Dean–Stark apparatus for azeotropic removal of water, forming during the condensation reaction. The reaction mixture was then cooled to room temperature and the solvent was rotary evaporated. The solid product so obtained was recrystallized from a mixture of chloroform and *n*-hexane (4:1).

6.2. Crystal structure determination

The triphenyltin (*E*)-3-(3-fluorophenyl)-2-(4-chlorophenyl)-2-propenoate, **5** was recrystallized from chloroform:*n*-hexane (4:1) on slow evaporation at room temperature.

A suitable colorless prismatic crystal of $C_{33}H_{24}ClFO_2Sn$ of the size $0.12 \times 0.10 \times 0.09$ mm^3 was coated with Paratone 8277 oil (Exxon) and mounted on a glass fiber. All measurements were made on a Nonius KappaCCD diffractometer with graphite monochromated Mo Kα radiation. Cell constants obtained from the refinement [36] of 15,288 reflections in the range $1.6° < \theta < 30.4°$ corresponded to a primitive triclinic cell; details of crystal data and structure refinement have been provided in Table 3. The data were collected [37] at a temperature of 173(2) K using the ω and φ scans to a maximum θ value of 30.4°. The data were corrected for Lorentz and polarization effects and for absorption using multi-scan method [36].

The structure was solved by the direct methods [38] and expanded using Fourier techniques [39]. The non-hydrogen atoms were refined anisotropically. F-atom was discovered over two *meta*-positions. Hydrogen atoms were included at geometrically idealized positions and were not refined. The final cycle of full-matrix least-squares refinement using SHELXL97 [40] converged with unweighted and weighted agreement factors, $R = 0.035$ and $wR = 0.074$ (all data), respectively, and goodness of fit, $S = 1.03$. The figures were plotted with the aid of ORTEPII [41]. CCDC deposition number: 248664.

6.3. Biocidal studies

Biological activity tests for the free acid and all synthesized compounds were carried out against various bacteria and fungi by the agar well diffusion method [29] and tube diffusion test [30], respectively. The toxicity of these compounds was determined by a brine-shrimp bioassay lethality method [32].

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