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SUPPLEMENTARY MATERIAL TO

Design, synthesis and biological evaluation of organotin(IV) complexes of flumequine and cetirizine

SYED HASSAN IFTIKHAR[1], SYEDA RUBINA GILANI[1], M. BABAR TAJ[2], AHMAD RAHEEL[2]*, IMTIAZ-UD-DIN[2], SYED AHMAD TERMIZI[2], MUNDHER AL-SHAKBAN[3] and HAPIPAH MOHD ALI[4]

[1]Department of Chemistry, University of Engineering and Technology, Lahore-54890, Pakistan, [2]Department of Chemistry, Quaid-i-Azam University, Islamabad 45320, Pakistan, [3]School of Chemistry, University of Manchester, M13 9PL, United Kingdom and [4]Department of Chemistry, University of Malaya, Kuala Lumpur, 50603, Malaysia

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*Trimethylstannyl 9-fluoro-6,7-dihydro-5-methyl-1-oxo-1*H,5H*-pyrido[3,2,1-*ij*]quinoline-2-carboxylate (**1**).* Quantities used were 0.261 g (0.001 mol) of **HL$_1$** and 0.18 g (0.001 mol) of trimethyltin hydroxide in toluene. Yield 72 %; m.p.: 107–110 °C; Anal. Calcd. for $C_{17}H_{20}O_3NFSn$ (FW: 424): C, 48.15; H, 4.75; N, 3.30; Sn, 27.99 %. Found: C, 48.20; H, 4.79; N, 3.31; Sn, 27.90 %; IR (KBr, cm^{-1}); 1641 (COO, asym.), 1464 (COO sym), $\Delta\nu$: 177, 523 (Sn–C), 442 (Sn–O); ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 9.02 (*s*, 1H, Ar–N–C**H**), 7.78 (*s*, 1H, **H**C–CF–Ar), 7.67 (s, 1H, C**H**-CF-Ar), 4.99–4.91 (*m*, 1H, –CH$_2$–C**H**N–CH$_3$), 3.14–3.08 (*m*, 2H, F–Ar–C**H**$_2$–CH$_2$), 2.16 (*d*, *J* = 8.5 Hz, 2H, –C**H**$_2$–CHN–CH$_3$), 0.93 (*d*, *J* = 8.2 Hz, 3H, –CH$_2$–CHN–C**H**$_3$), 0.52 (*s*, 9H, **H**$_3$C–Sn); ^{13}C-NMR (75.45 MHz, DMSO-d_6, δ / ppm): 178.1 (Ar-C=O), 161.2 (COO), 148.7, 146.0, 127.6, 127.4, 127.1, 126.9, 126.7 (Ar-C), 122.2, 58.5, 26.4, 22.3, 20.7 (CH$_2$-flumequine), 15.03 (Sn–CH$_3$); ^{119}Sn-NMR (129 MHz, DMSO-d_6, δ / ppm): –142.6; MS (*m*/*z*): 425 $[C_{17}H_{20}O_3NFSn]^+$ (M+1).

*Tributylstannyl 9-fluoro-6,7-dihydro-5-methyl-1-oxo-1*H,5H*-pyrido[3,2,1-*ij*]quinoline-2-carboxylate (**2**).* Quantities used were 0.261 g (0.001 mol) of **HL$_1$** and 0.291 g (0.001 mol) of tributyltin hydroxide in toluene. Yield 66 %; m.p.: 142–145 °C. Anal. Calcd. for $C_{26}H_{38}O_3NFSn$ (MW = 550): C, 56.75; H, 6.96; N, 2.55; Sn, 21.57 %; Found: C, 56.71; H, 6.99; N, 2.59; Sn, 21.60 %. IR (KBr disc, cm^{-1}); ν_{asym}(COO) 1648, ν_{sym}(COO) 1463, $\Delta\nu$ = 185, 521 (Sn–C), 449 (Sn–O). ^{1}H-NMR (400 MHz,DMSO-d_6, δ / ppm): 9.01 (*s*, 1H, Ar–N–C**H**), 7.77 (*s*, 1H, **H**C–CF–Ar), 7.64 (*s*, 1H, C**H**–CF–Ar), 4.91–4.87 (*m*, 1H, –CH$_2$–C**H**N–CH$_3$),

* Corresponding author. E-mail: ahmadraheel001@gmail.com

3.10–3.06 (*m*, 2H, F–Ar–C**H**$_2$–CH$_2$), 2.16 (*d*, *J* = 8.5 Hz, 2H, –C**H**$_2$–CHN–CH$_3$), 0.93 (*d*, *J* = 8.2 Hz, 3H, –CH$_2$–CHN–C**H**$_3$), 1.53–1.27 (*m*, 18H, CH$_2$, Bu), 0.72––0.68 (*m*, 9H, **H**$_3$C of Bu); ^{13}C-NMR (75.45 MHz, DMSO-d_6, δ / ppm): 176.5 (Ar-**C**=O), 163.7 (**C**OO), 148.2, 146.0, 127.3, 127.1, 126.8, 126.5, 126.3 (Ar-**C**), 122.1, 58.5, 46.4, 26.2, 25.3, 22.1, 20.3 (CH$_2$-flumequine and Bu), 16.23 (H$_3$**C** of Bu). ^{119}Sn-NMR (129 MHz, DMSO-d_6, δ / ppm): –119.6. (*m*/*z*) (M+1) peak $[C_{26}H_{38}O_3NFSn]^+$ (551).

*Triphenylstannyl 9-fluoro-6,7-dihydro-5-methyl-1-oxo-1*H,*5*H-*pyrido[3,2,1-*-ij*]quinoline-2-carboxylate (**3**)*. Quantities used were 0.261 g (0.001 mol) of **HL$_1$** and 0.367 g (0.001 mol) of triphenyltin hydroxide in toluene. Yield 68 %; m.p.: 161–163 °C. Anal. Calcd. for $C_{32}H_{26}O_3NFSn$ (MW = 611): C, 62.98; H, 4.29; N, 2.30 %; Found: C, 62.94; H, 4.29; N, 2.31 %. IR (KBr disc, cm^{-1}): ν_{asym}(COO) 1685, ν_{sym}(COO) 1432, $\Delta\nu$ = 253, 519 (Sn–C), 446 (Sn–O). ^{1}H-NMR (400 MHz, DMSO-d_6, δ / ppm): 8.97 (*s*, 1H, Ar–N–C**H**), 7.76 (*s*, 1H, **H**C–CF–Ar), 7.64 (*s*, 1H, C**H**–CF–Ar), 7.59–7.32 (*m*, 15H, Ph–Sn), 4.95–4.87 (*m*, 1H, –CH$_2$–C**H**N–CH$_3$), 3.12–3.07 (*m*, 2H, F–Ar–C**H**$_2$–CH$_2$), 2.16 (*d*, *J* = 8.5 Hz, 2H, –C**H**$_2$–CHN–CH$_3$), 0.93 (*d*, *J* = 8.2 Hz, 3H, –CH$_2$–CHN–C**H**$_3$); ^{13}C-NMR (75.45 MHz, DMSO-d_6, δ / ppm): 171.1 (Ar-**C**=O), 163.2 (**C**OO), 148.1, 145.7, 131.4, 133.8, 133.3, 132.9.132.2, 127.6, 127.4, 127.1, 126.9, 126.7 (Ar-C), 122.2, 58.0, 26.4, 22.3, 20.2 (CH$_2$-flumequine). ^{119}Sn-NMR(129 MHz, DMSO-–d_6, δ / ppm): –35.2. (*m*/*z*) (M+1) peak $[C_{32}H_{26}O_3NFSn]^+$ (612).

*Trimethylstannyl 2-[2-[4-[(4-chlorophenyl)phenylmethyl]piperazin-1-yl]ethoxy]acetate (**4**)*. Quantities used were 0.461 g (0.001 mol) of **HL$_2$** and 0.18 g (0.001 mol) of trimethyltin hydroxide in toluene. Yield 65 %; m.p.: 150–153 °C. Anal. Calcd. for $C_{24}H_{33}O_3N_2ClSn$ (MW = 552): C, 52.25; H, 6.03; N, 5.08; Cl, 6.43 Sn, 21.52 %; Found: C, 52.30; H, 6.05; N, 5.10; Cl, 6.40; Sn, 21.50 %. IR (KBr disc, cm^{-1}); ν_{asym}(COO) 1642, ν_{sym}(COO) 1466 , $\Delta\nu$ = 176, 522 (Sn–C), 447 (Sn–O).^{1}H-NMR (400 MHz,DMSO-d$_6$ δ/ ppm): 7.60–7.54 (*m*, 4H, Cl-Ar), 7.48––7.40 (*m*, 5H, Ar), 5.09 (*s*, 1H, Ar(N)C**H**–CCl–Ar), 4.15 (*s*, 2H, –O–**H**$_2$C–COO), 3.82 (*t*, *J* = 6.7 Hz, 2H, O–C**H$_2$**–CH$_2$–N), 3.68 (*t*, *J* = 6.4 Hz, 2H, O–CH$_2$–C**H$_2$**–N), 3.47–3.41 (*m*, 4H, N–C**H$_2$**C**H$_2$**–N), 3.37–3.31 (*m*, 4H, N–C**H$_2$**C**H$_2$**–N), 0.56 (s, 9**H**, H$_3$C–Sn); ^{13}C-NMR (75.45 MHz, DMSO-d_6, δ/ ppm): 173.8 (**C**OO), 134.9, 133.7, 132.8, 130.5.130.2, 129.9, 129.6, 128.0, 127.8, 127.6, 127.4, 127.2 (Ar-C), 74.5, 66.7, 63.5, 56.2, 48.4, 48.2, 47.9, 47.7, 13.5 (H$_3$**C**-Sn). ^{119}Sn-NMR DMSO-d_6, δ / ppm): –101.6. (*m*/*z*) (M+1) peak $[C_{24}H_{33}O_3N_2ClSn]^+$ (553), (M+2) peak $[C_{24}H_{33}O_3N_2ClSn]^+$ (554).

*Tributylstannyl 2-[2-[4-[(4-chlorophenyl)phenylmethyl]piperazin-1-yl]ethoxy]acetate (**5**)*. Quantities used were 0.461 g (0.001 mol) of **HL$_2$** and 0.291 g (0.001 mol) of tributyltin hydroxide in toluene. Yield 68 %; m.p. 137–140 °C. Anal. Calcd. for $C_{33}H_{51}O_3N_2ClSn$ (MW = 678): C, 58.45; H, 7.60; N, 4.15; Cl, 5.25 Sn, 17.50%; Found: C, 58.50; H, 7.56; N, 4.17; Cl, 5.28; Sn, 17.55 %. IR

(KBr disc, cm^{-1}); ν_{asym}(COO) 1650, ν_{sym}(COO)1457 , $\Delta\nu$ = 193 , 519 (Sn–C), 443 (Sn–O). ^{1}H-NMR (400 MHz,DMSO-d_6 , δ / ppm): 7.64–7.58 (*m*, 4H, Cl–Ar), 7.52–7.44 (*m*, 5H, Ar), 5.12 (*s*, 1H, Ar(N)C**H**–CCl–Ar), 4.19 (*s*, 2H, –O–**H**$_2$C–COO), 3.82 (*t*, *J* = 6.7 Hz, 2H, O–C**H**$_2$**–**CH$_2$–N), 3.68 (*t*, *J* = 6.4 Hz, 2H, O–CH$_2$**–**C**H**$_2$–N), 3.51–3.45 (*m*, 4H, N–C**H**$_2$C**H**$_2$–N), 3.39–3.32 (*m*, 4H, N–C**H**$_2$C**H**$_2$–N), 1.51–1.23 (*m*, 18H, CH$_2$, Bu), 0.81–0.75 (*m*, 9**H**, H$_3$C of Bu); ^{13}C-NMR (75.45 MHz, DMSO-d_6, δ / ppm): 173.8 (**C**OO), 134.9, 133.7, 132.8, 130.5.130.2, 129.9, 129.6, 128.0, 127.8, 127.6, 127.4, 127.2 (Ar-C), 74.5, 66.7, 63.5, 56.2, 48.4, 48.2, 47.9, 47.7, 42.23, 26.12, 21.05 (CH$_2$,Bu), 15.53 (H$_3$**C** of Bu). ^{119}Sn-NMR DMSO-d_6, δ / ppm): –159.7. (*m*/*z*) (M+1) peak $[C_{33}H_{51}O_3N_2ClSn]^+$ (679), (M+2) peak $[C_{33}H_{51}O_3N_2ClSn]^+$ (680).

*Triphenylstannyl 2-[2-[4-[(4-chlorophenyl)phenylmethyl]piperazin-1-yl]ethoxy]acetate (**6**)*. Quantities used were 0.461 g (0.001 mol) of **HL$_2$** and 0.367 g (0.001 mol) of triphenyltin hydroxide in toluene. Yield 61 %; m.p.: 168–170 °C. Anal. Calcd. for $C_{39}H_{39}N_2O_3ClSn$ (MW 737): C, 63.48; H, 5.33; N, 3.80; Cl, 4.80 Sn, 16.10 %; Found: C, 63.55; H, 5.35; N, 3.82; Cl, 4.78; Sn, 16.15 %. IR (KBr disc, cm^{-1}); ν_{asym}(COO) 1687, ν_{sym}(COO) 1436, $\Delta\nu$ = 251, 525 (Sn–C), 452(Sn–O). ^{1}H-NMR (400 MHz,DMSO-d_6, δ / ppm): 7.74–7.66 (*m*, 4H, Cl–Ar), 7.59––7.22 (*m*, 20H, Ph+Ph–Sn), 5.13 (*s*, 1H, Ar(N)C**H**–CCl–Ar), 4.14 (*s*, 2H, –O–**H**$_2$C–COO), 3.82 (*t*, *J* = 6.7 Hz, 2H, O–C**H**$_2$**–**CH$_2$–N), 3.68 (*t*, *J* = 6.4 Hz, 2H, O–CH$_2$**–**C**H**$_2$–N), 3.44–3.38 (*m*, 4H, N–C**H**$_2$C**H**$_2$–N), 3.32–3.26 (*m*, 4H, N–C**H**$_2$C**H**$_2$–N); ^{13}C-NMR (75.45 MHz, DMSO-d_6, δ / ppm): 173.8 (**C**OO), 134.9, 133.7, 132.8, 130.5, 130.2, 129.9, 129.6, 128.0, 127.8, 127.6, 127.4, 127.2, 126.9, 126.4, 125.8, 125.3, 124.9 (Ar-C), 74.5, 66.7, 63.5, 56.2, 48.4, 48.2, 47.9, 47.7. ^{119}Sn-NMR DMSO-d_6, δ / ppm): –21.8. (*m*/*z*) (M+1) peak $[C_{39}H_{39}N_2O_3ClSn]^+$ (738), (M+2) $[C_{39}H_{39}N_2O_3ClSn]^+$ peak (739).

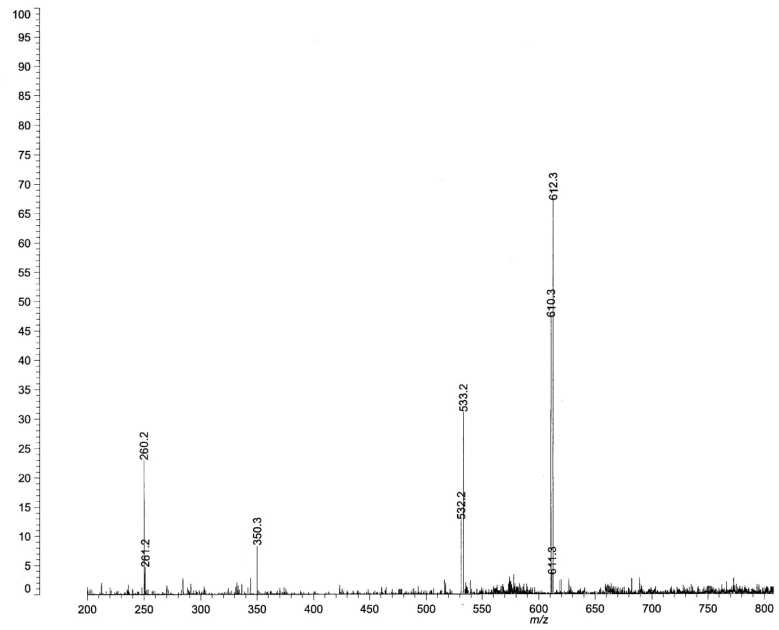

Fig. S-1. Mass spectrum of compound **3**.

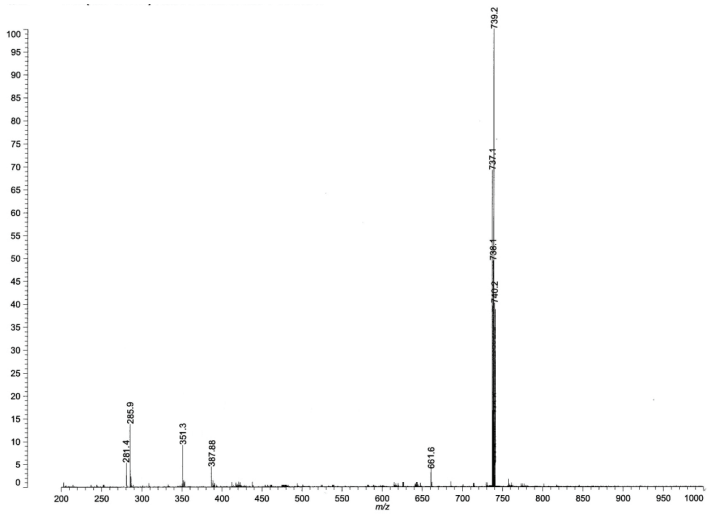

Fig. S-2. Mass spectrum of compound **6**.

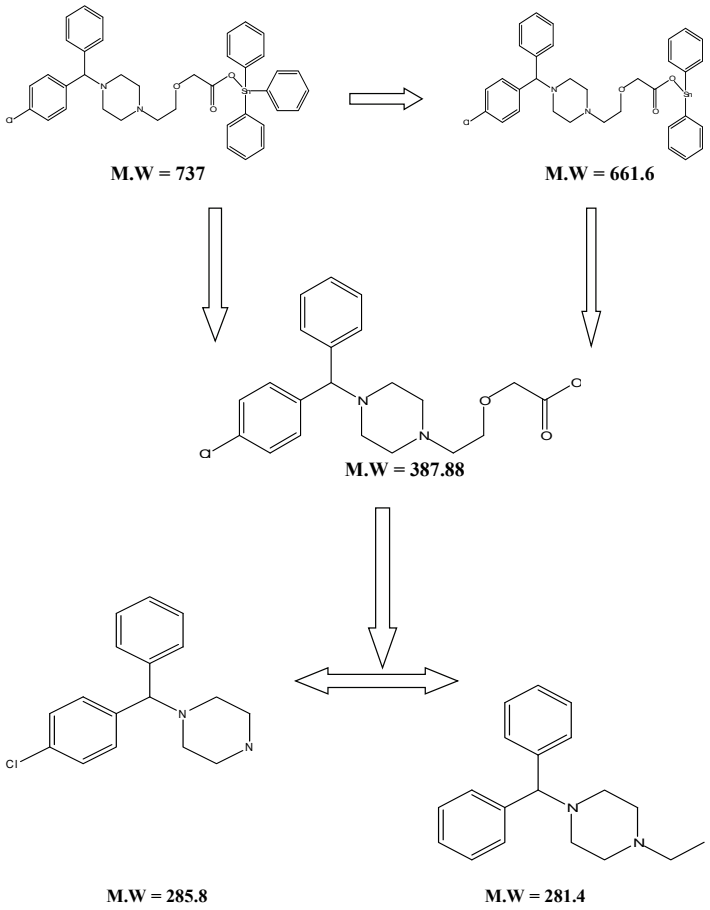

Fig. S-3. Fragmentation pattern of triphenyltin(IV) (**L_2**) carboxylates (compound **6**).

ANTIOXIDANT

TABLE S-I. Antioxidant activity data

Compound		Inhibition[a], %	IC_{50} / μM
$(CH_3)_3Sn(L_1)$	(**1**)	86.29±2.0	19±1
$(C_4H_9)_3Sn(L_1)$	(**2**)	60.30±1.5	53±2
$(C_6H_5)_3Sn(L_1)$	(**3**)	52.30±1.0	55±3
$(CH_3)_3Sn(L_2)$	(**4**)	91.35±2.1	20±1
$(C_4H_9)_3Sn(L_2)$	(**5**)	59.35±1.3	56±3
$(C_6H_5)_3Sn(L_2)$	(**6**)	51.90±1.0	59±3
Ligand (HL_1)	(**7**)	58.50±1.0	43±1
Ligand (HL_2)	(**8**)	63.40±1.2	48±2
Gallic acid	(**9**)	92.90±1.0	14±1

[a]100 μL samples (5 mg/mL in DMSO)

TABLE S-II. Data of DNA binding studies ($(\eta/\eta_o)^{1/3}$) by viscosity method

Binding ratio [Compound]/[SS-DNA]	Compound							
	HL_1	**HL_2**	**1**	**2**	**3**	**4**	**5**	**6**
0.0	1.025	1.03	1.025	1.025	1.025	1.03	1.03	1.03
0.25	1.026	1.03	1.035	1.036	1.038	1.038	1.038	1.038
0.55	1.03	1.033	1.043	1.045	1.046	1.046	1.046	1.046
0.80	1.05	1.055	1.052	1.064	1.067	1.055	1.067	1.072
1.15	1.06	1.065	1.072	1.073	1.074	1.076	1.076	1.076
1.40	1.075	1.076	1.095	1.095	1.095	1.10	1.10	1.10

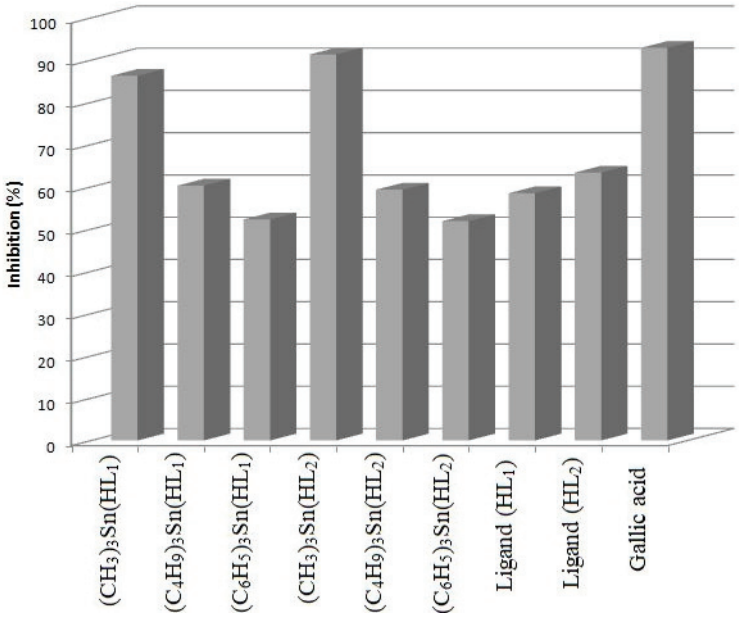

Fig. S-4. Antioxidant activity of compounds, ligands and standard.

TABLE S-III. Antibacterial activities of ligands and complexes; zone of inhibition, mm; concentration: 1 mg/mL of DMSO. Reference drug: cefixime, 1 mg/mL

Compound	Bacterium				
	Escherichia coli	*Bacillus subtilis*	*Staphylococcus aureus*	*Pseudomonas aeruginosa*	*Micrococcus luteus*
Ligand (HL_1)	10	08	09	10	11
Ligand (HL_2)	11	10	11	11	11
$(CH_3)_3Sn(L_1)$ (**1**)	13	11	14	15	14
$(C_4H_9)_3Sn(L_1)$ (**2**)	14	12	13	13	15
$(C_6H_5)_3Sn(L_1)$ (**3**)	15	13	13	14	13
$(CH_3)_3Sn(L_2)$ (**4**)	13	14	12	15	14
$(C_4H_9)_3Sn(L_2)$ (**5**)	11	12	13	14	13
$(C_6H_5)_3Sn(L_2)$ (**6**)	12	15	12	12	15
Cefixime	22	21	19	20	23

TABLE S-IV. Antifungal activity data, growth inhibition, %; agar tube dilution method, concentration: 200 mg/mL of DMSO

Compound	Fungus		
	Trichophyton longiformis	*Candida albicans*	*Aspergillus flavus*
Ligand (HL_1)	07	10	15
Ligand (HL_2)	10	09	16
$(CH_3)_3Sn(L_1)$ (**1**)	12	10	18
$(C_4H_9)_3Sn(L_1)$ (**2**)	13	11	17
$(C_6H_5)_3Sn(L_1)$ (**3**)	13	10	18
$(CH_3)_3Sn(L_2)$ (**4**)	14	13	17
$(C_4H_9)_3Sn(L_2)$ (**5**)	13	14	16
$(C_6H_5)_3Sn(L_2)$ (**6**)	12	13	19
Terbinafine	21	23	28

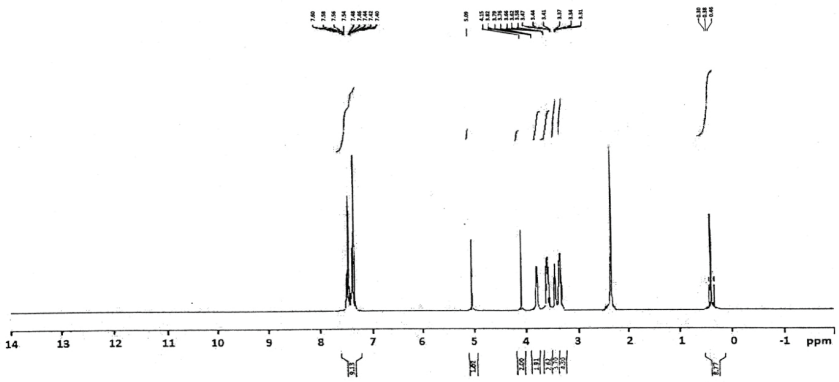

Fig. S-5. ^{1}H-NMR of complex **4**.

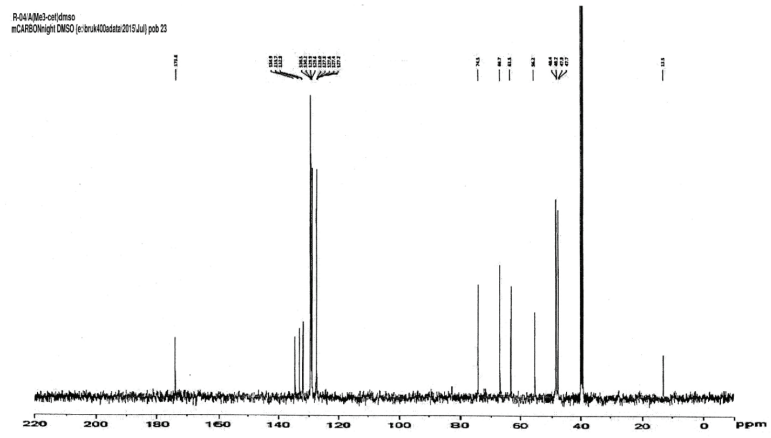

Fig. S-6. ^{13}C-NMR of complex **4**.

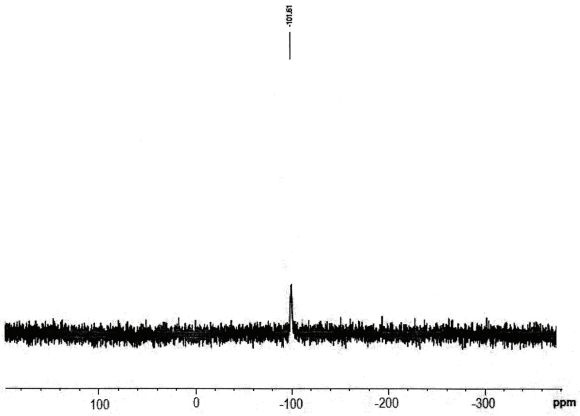

Fig. S-7. ^{119}Sn-NMR of complex **4**.

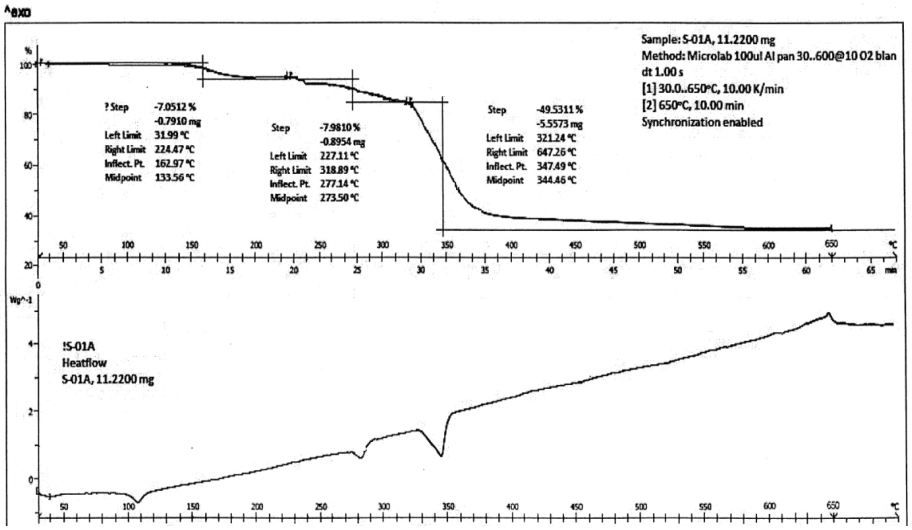

Fig. S-8. TGA-DSC graph of complex **1**.