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Dedicated to Professor Luminița Silaghi-Dumitrescu on the occasion of her 65th anniversary

NOVEL 1,9-DIACYL-5-(PHENOTHIAZINYL)DIPYRROMETHANE DIALKYLTIN COMPLEXES

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ABSTRACT New 1,9-diacyl-5-(phenothiazinyl)dipyrromethane (aphdpm) obtained by diacylation of 5-phenothiazinyl-dipyrromethane were subjected to complexation reactions with dimethyl- and di-*n*-butyltin(IV) dichloride which afforded complexes of the type [Me_2Sn(aphdpm)] and [(*n*-Bu)$_2$Sn(aphdpm)] respectively [where aphdpm: 1,9-diformyl-5-(phenothiazinyl)dipyrromethane and 1,9-dibenzoyl-5-(phenothiazinyl) dipyrromethane]. Plausible structures of the new tin(IV) complexes were proposed based on spectroscopic FT-IR, ^{1}H-,^{13}C-,^{119}Sn-NMR and mass spectrometry studies.

Keywords: *Dipyrromethane, Phenothiazine, Tin complexes*

INTRODUCTION

Dipyrromethanes bearing acyl groups at the α positions of the pyrrole units are key precursors to porphyrins with diverse substituents in the *meso* positions and thus the synthetic procedures gained additional importance. Taking benefit from the electron rich nature of the pyrrole units, substitution was readily achieved in the presence of mild electrophiles. Thus, Vilsmeier formylation [1] and benzoylation procedures were applied in the preparation of acyl-dipyrromethanes [2] producing both mono- and diacylated dipyrromethanes

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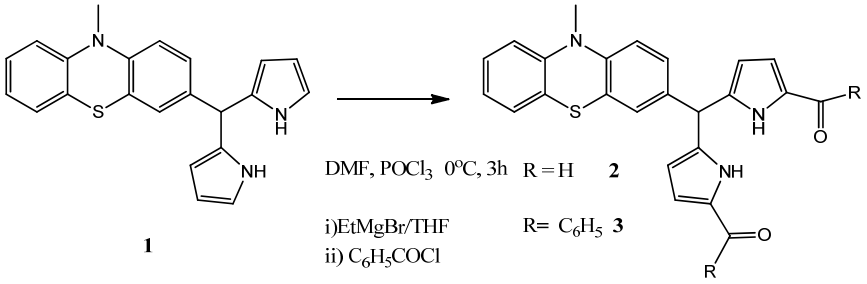
with high regioselectivity for the α positions of the pyrrole rings. The treatment of a dipyrromethane with ethylmagnezium bromide in THF followed by the reaction of the pyrrolate intermediate with acid chloride also generated a mixture of mono- and diacylated dipyrromethane [3]. Optimization of the reaction conditions (reagents ratio, solvent, temperature) afforded increased ratio of diacylated : monoacylated derivatives (5:1) [4].

The properties of the dipyrromethanes can be conveniently modulated by the presence of various structural motifs in the *meso* position (methylene bridge) and/or by introducing different substituents in the α positions of the pyrrole units. The current interest on organotin(IV) complexes lays on a wide range of applications [5] such as catalysts, biocides [6] or antitumor agents [7]. 1,9-Diacyldipyrromethane-tin complexes were reported to be formed selectively from a crude acylation mixture upon treatment with dibutyltin dichloride [8].

Dipyrromethane derivatives functionalized in the *meso* position with phenothiazine units were first reported by our research group [9] and in this work we focus on their chemical characterization by describing the acylation and tin complexation of 1,9-diacyl-phenothiazinyl-dipyrromethanes ligands. Taking into consideration the biological activity potential of the individual heterocyclic units embedded in their structure, we consider the new phenothiazine functionalized dipyrromethane derivatives as stimulating structures for applications in biological systems.

RESULTS AND DISCUSSION

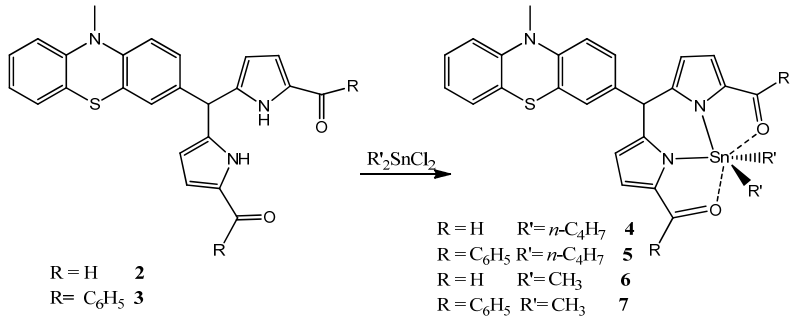
The reactivity of the starting phenothiazinyl-dipyrromethanes **1** is governed by the presence of two types of electron rich heteroaromatic units susceptible of readily undergoing electrophilic substitution under the influence of mild electrophiles. Careful selection of the reaction conditions was required for increasing the regioselectivity. The synthesis of 1,9-diformyl-phenothiazinyl-dipyrromethane **2** and 1,9-dibenzoyl-phenothiazinyl-dipyrromethane **3** are presented in Scheme 1. Vilsmeier formylation performed at 0^{o}C offered a high regioselectivity towards the α positions of the pyrrole units generating diformyl derivative **2** in 65% yields. 1,9-dibenzoyl-phenothiazinyl-dipyrromethane **3** was prepared in 45% yields by a two steps procedure which implied the treatment of the starting phenothazinyl-dipyrromethane with ethylmagnesium bromide, followed by the reaction of dipyrromethane analog of the "pyrrole Grignard reagent," with benzoyl chloride.



Scheme 1

The FT-IR analysis of the acylation products **2** and **3** displayed the absorption band corresponding to the stretching vibration of the carbonyl bonds situated at 1650 cm^{-1}.

The reaction of diacyl derivatives **2, 3** with dibutyltin dichloride and dimethyltin dichloride respectively, afforded the corresponding tin complexes **2**$SnBu_2$ **4**, **3**$SnBu_2$ **5, 2**$SnMe_2$ **6** and **3**$SnMe_2$ **7** (scheme 2) which were isolated by passage through a silica pad followed by precipitation from methanol.



Scheme 2

The structural assignments of the complexes were based on FT-IR, ^{1}H-, ^{13}C- and ^{119}Sn-NMR spectroscopy and high resolution mass spectrometry studies. The molecular weight of each complex **4-7** was determined from the HRMS(APCI+) spectrum which displayed the molecular ion in high abundance. In the IR domain the main spectral changes included the disappearance of the IR stretching vibrations of the N-H bonds of the ligands and the shifting of the characteristic stretching vibration of the carbonyl bonds towards lower wavenumber values. Deeper structural assignments of dialkyltin complexes **4-7** were achieved based on 2D-NMR homonuclear correlation

(H-H COSY) and heteronuclear (HMQC) experiments. Upon complexation, the protons attached to the pyrrole units appeared more shielded (chemical shift values with additional 0.3–0.2 ppm), but only a negligible effect of the environment was recorded for the protons of the phenothiazine unit situated in the *meso* position. The alkyl groups connected to the tin atom gave two sets of signals in both ^{1}H- and ^{13}C-NMR spectra according to their *syn* or *anti* spatial position with respect to the *meso*-substituent.

For each complex **4-7** the decoupled ^{119}Sn-NMR spectrum displayed a signal situated in the range from -219 ppm to -272 ppm. An upfield shift of the chemical shift value was observed as a result of a structural change of the alkyl substituent from dibutyl to dimethyl group, as well as in the case of a change of the acyl group from benzoyl to formyl group (figure 1). The undecoupled ^{119}Sn-NMR spectra revealed multiplet signals with splitting patterns mainly governed by the vicinal heteronuclear coupling constants ^{119}Sn-^{1}H of about 80 Hz.

A correlation between the range of the chemical shift values recorded in the ^{119}Sn-NMR spectra of different coordination butyltin complexes with the coordination numbers of the central tin atom was previously described, offering the possibility to assign the coordination geometry around the central tin atom [10]. Based on the evidence that six-coordinate compounds are producing chemical shifts values ranging from −210 to −400 ppm, we assumed an octahedral coordination geometry for each of the complexes **4-7.**

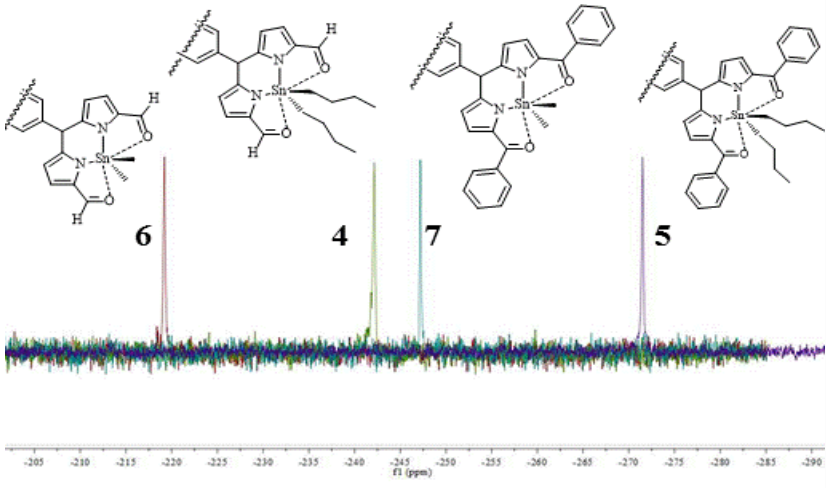


Figure 1. 149 MHz ^{119}Sn-NMR spectra of 1,9-diacyl-5-(phenothiazinyl)-dipyrromethane dialkyltin complexes

CONCLUSIONS

Synthetic procedures for the preparation of novel 1,9-diacyl-phenothiazinyl-dipyrromethane derivatives based on Vilsmeier formylation and acylation with benzoyl chloride respectively, were described.

New [diacyl-5-(phenothiazine-3-yl)dipyrromethane]-dialkytin complexes were obtained and their structure was confirmed by high resolution spectroscopic techniques (FT-IR, ^{1}H-, ^{13}C-, ^{119}Sn-NMR spectroscopy and HRMS). An octahedral coordination geometry of the central tin atom was sustained by literature data regarding the plausible correlation between the ^{119}Sn-NMR chemical shifts and the coordination geometry of butyltin complexes.

EXPERIMENTAL SECTION

All chemicals used were of reagent grade. The melting points were determined in capillaries with an Electrothermal 9100 instrument. HRMS spectra were recorded on a Thermo LTQ *Orbitrap XL* with ESI+ ionization mode. NMR spectra were recorded in solution at room temperature on a 400 and 600 MHz Bruker Avance instrument. Chemical shifts are expressed in terms of δ (ppm) relative to standard tetramethylsilane (TMS). FT-IR spectra were recorded in KBr pellet using a Bruker Vector 22 instrument.

5-(phenothiazinyl)dipyrromethane: 1 was prepared according to our previously reported procedure [9].

Synthesis of 5,5'-((10-methyl-10*H*-phenothiazin-3-yl)methylene)bis(1*H*-pyrrole-2-carbaldehyde) (**2**). DMF (10 mL) was treated with $POCl_3$ (1 mL, 10.2 mmol) at 0°C under argon, and the resulting solution was stirred for 10 min (Vilsmeier reagent). A solution of 1 (1.00 g, 2.8 mmol) in DMF (15 mL) at 0°C under argon was treated with the freshly prepared Vilsmeier reagent, and the resulting solution was allowed to stir for 1.5 h at 0°C. Saturated aqueous sodium acetate solution (100 mL) was added, and the ice bath was removed. The mixture was then stirred for 4 h and allowed to warm to room temperature. The mixture was extracted with ethyl acetate. The collected organic phase was washed with brine, dried with $MgSO_4$, and filtered. The filtrate was concentrated to dryness under reduced pressure. The crude product was purified by column chromatography (using silica gel and DCM/MeOH ratio 20/1 as eluent), the product is a brown-yellow solid, 65% yield, m.p. 192-194 ^{o}C (decomp.); MS (ESI+): 414 [M+H^{+}], 396; ^{1}H-NMR (400MHz, $CDCl_3$): δ ppm: 3.35 (s, 3H, N-CH_3-), 5.47 (s, 1H, H_5), 6.04 (m, 2H, $H_{3,7}$), 6.74 (d, 1H, $H_{1'}$, ^{3}J= 8.8Hz), 6.81-6.83 (m, 3H, $H_{9'}$, $H_{2,8}$), 6.94 (t, 1H, $H_{7'}$, ^{3}J= 7.3 Hz), 7.02- 7.05 (m, 2H, $H_{4',2'}$), 7.12 (d, 1H, $H_{6'}$, ^{3}J= 7.3 Hz), 7.18 (t, 1H, $H_{8'}$, ^{3}J= 7.3 Hz), 9.18 (s, 2H, $H_{1a,9a}$), 10.52 (brs, 2H, $H_{10,11}$); ^{13}C-NMR (100 MHz, $CDCl_3$):

δppm= 35.3 (CH, C_a), 43.4 (CH, C_5), 111.4 (CH, $C_{3,7}$), 114.1 (CH, $C_{9'}$), 114.2 (CH, $C_{1'}$), 122.2 (CH, $C_{2,8}$), 122.6 (CH, $C_{7'}$), 122.9 (Cq, $C_{4a'}$), 124 (Cq, $C_{5a'}$), 126.9 (CH, $C_{4'}$), 127.2 (CH, $C_{2'}$), 127.4 (CH, $C_{6'}$), 127.5 (CH, $C_{8'}$), 132.6 (Cq, $C_{3,6}$), 133.3 (Cq, $C_{3'}$), 141.3 (Cq, $C_{1,9}$), 145.3 (Cq, $C_{9a'}$), 145.5 (Cq, $C_{10a'}$), 178.9 (Cq, $C_{1a,9a}$); IR (KBr): ū(cm^{-1}): 3243, 2970, 2815, 1650, 1488, 1352, 1287, 1254, 1111, 786, 747, 669.

(5,5'-((10-methyl-10H-phenothiazin-3-yl)methylene)bis(1H-pyrrole-5,2-diyl))*bis*(phenylmethanone) (3). A solution of EtMgBr (35 mL, 35 mmol, 1.0M solution in THF) was added slowly to a water cooled flask containing a solution of 5-(phenothiazinyl)dipyrromethane (2.5 g, 7 mmol) in toluene (200 mL) under argon. An exothermic reaction with gas evolution was observed. The resulting mixture was stirred at room temperature for 30 min. A solution of benzoyl chloride (4.07 mL, 35 mmol) in toluene (25 mL) was added over 10 min, and the resulting solution was further stirred for 10 min. The reaction mixture was poured into saturated aqueous NH_4Cl (200 mL) and ethyl acetate (150 mL). The organic layer was washed with water and brine, dried $MgSO_4$, and filtered. The filtrate was concentrated to dryness under reduced pressure. The crude product was purified by column chromatography (using silica gel and DCM/MeOH ratio 40/1 as eluent) and afforded the product as a brown solid in 48% yield, m.p. 114 ºC (decomp.); MS (ESI+): 566 [$M+H^+$], 457, 390, 274; ^{1}H-NMR (400MHz, $CDCl_3$): δppm: 3.37 (s, 3H, H_a), 5.63 (s, 1H, H_5), 6.01 (m, 2H, $H_{3,7}$), 6.56 (m, 2H,, $H_{2,8}$), 6.77 (d, 1H, $H_{1'}$, ^{3}J= 8.3 Hz), 6.84 (d, 1H, $H_{9'}$, ^{3} J= 8.1 Hz), 6.95 (t, 1H, $H_{7'}$, ^{3}J= 7.5 Hz), 7.12 (d, 1H, $H_{6'}$, ^{3} J= 7 Hz), 7.19 (t, 1H, $H_{8'}$, ^{3}J= 7 Hz), 7.27-7.30 (m, 1H, $H_{2',4'}$), 7.38-7.42 (m, 4H, $H_{c'}$), 7.49-7.52 (m, 2H, $H_{d'}$), 7.79 (d, 4H, $H_{b'}$, ^{3}J= 7.3 Hz), 11.68 (brs, 2H, $H_{10,11}$); ^{13}C-NMR (100 MHz, $CDCl_3$): δppm: 35.3 (CH, C_a), 44 (CH, C_5), 111.1 (CH, $C_{3,7}$), 114 (CH, $C_{9'}$), 114.2 (CH, $C_{1'}$), 120.9 (CH, $C_{2,8}$), 122.5 (CH, $C_{7'}$), 123.2 (Cq, $C_{4a'}$), 124 (Cq, $C_{5a'}$), 127.2 (CH, $C_{4'}$), 127.4 (CH, $C_{2'}$), 127.5 (CH, $C_{6'}$), 127.7 (CH, $C_{8'}$), 128 (CH, $C_{c'}$), 129 (CH, $C_{d'}$), 129.6 (CH, $C_{b'}$), 131 (Cq, $C_{a'}$), 131.6 (Cq, $C_{4,6}$), 138.2 (Cq, $C_{3'}$), 141.01 (Cq, $C_{1a,9a}$), 145.1 (Cq, $C_{9a'}$), 145.7 (Cq, $C_{10a'}$), 184.5 (Cq, $C_{1a,9a}$); IR (KBr): ū(cm^{-1}): 3433, 3262, 2957, 2871, 1596, 1567, 1463, 1401, 1332, 1289, 1237, 928, 774, 728, 696;

General procedure for Tin Complexation of 1,9-diacyl-dipyrro-methanes. A crude sample of phenothyazinyl-1,9-diacyldipyrromethane (**2, 3**) (2 mmol) was treated with TEA (6 mmol) and R'_2SnCl_2 (2 mmol) in DCM (4 mL) at room temperature and left to stand overnight. The mixture was filtered over a short pad of silica eluted with DCM. The eluent was concentrated to dryness. The residue was dissolved in a minimum amount of diethyl ether, and then methanol was added, yielding a precipitate, which upon filtration afforded a colorless/rose solid (65-80%).

5,5-dibutyl-10-(10-methyl-10H-phenothiazin-3-yl)-5,10-dihydrodipyrrolo [1,2-c:2',1'-f][1,3,2]diazastannine-3,7-dicarbaldehyde (4). Column chromatography (DCM), MeOH precipitation, afforded the product as a white solid in 78% yields, m.p. 97-99 ºC (decomp.); MS (ESI+): 646 [$M+H^+$]; ^{1}H-NMR (600MHz, $CDCl_3$): δppm= 0.75

(t, 3H, $H_{\delta'}$, ^{3}J= 7.32 Hz), 0.83 (t, 3H, H_{δ}, ^{3}J= 7.32 Hz), 1.14-1.18 (m, 2H, $H_{\gamma'}$), 1.28-1.34 (m, 4H, $H_{\gamma,\beta'}$), 1.45-1.48 (m, 4H, $H_{\beta,\alpha'}$), 1.62-1.66 (m, 2H, H_{α}), 3.35 (s, 3H, H_a), 5.46 (s, 1H, H_{10}), 6.18 (d, 2H, $H_{1,9}$, ^{3}J= 3.8 Hz), 6.73 (d, 1H, $H_{1'}$, ^{3}J= 8.3 Hz), 6.80 (d, 1H, $H_{9'}$, ^{3}J= 8 Hz), 6.91 (d, 1H, $H_{4'}$, ^{4}J= 2 Hz), 6.93 (td, 1H, $H_{7'}$, ^{4}J= 0.8 Hz, ^{3}J= 7.5 Hz), 6.96 (dd, 1H, $H_{2'}$, ^{4} J= 1.3 Hz, ^{3}J= 8.3 Hz), 7.08 (d, 2H, $H_{2,8}$, ^{3}J= 3.8 Hz), 7.12 (dd, 1H, $H_{6'}$, ^{4}J= 1.3 Hz, ^{3}J= 7.6 Hz), 7.17 (td, 1H, $H_{8'}$, ^{4}J= 1.3 Hz, ^{3}J= 8.2 Hz), 9.18 (s, 2H, $H_{1,9}$); ^{13}C-NMR (125 MHz, $CDCl_3$): δppm= 13.4 (CH, $C_{\delta'}$), 13.6 (CH, C_{δ}), 23.9 (CH, C_{α}), 24.4 (CH, $C_{\gamma'}$), 26 (CH, C_{γ}), 26.4 (CH, $C_{\alpha'}$), 27 (CH, $C_{\beta'}$), 27.2 (CH, C_{β}), 35.2 (CH, C_a), 44.2 (CH, C_{10}), 114.03 (CH, $C_{9'}$), 114.08 (CH, $C_{1'}$), 115.4 (CH, $C_{1,9}$), 122.5 (CH, $C_{7'}$), 123 (Cq, $C_{4a'}$), 123.8 (Cq, $C_{5a'}$), 123.9 (CH, $C_{2,8}$), 126.5 (CH, $C_{4'}$), 126.9 (CH, $C_{6'}$), 127.1 (CH, $C_{2'}$), 127.5 (CH, $C_{8'}$), 137.93 (Cq, $C_{9a,10a}$), 137.98 (Cq, $C_{3'}$), 144.6 (Cq, $C_{9a'}$), 145.6 (Cq, $C_{10a'}$), 151.9 (Cq, $C_{3,7}$), 178.6 (Cq, $C_{1a,9a}$); ^{119}Sn-NMR (149 MHz, $CDCl_3$): δppm= - 242.16.

5,5-dimethyl-10-(10-methyl-10H-phenothiazin-3-yl)-5,10-dihydrodipyrrolo [1,2-c:2',1'-*f*][1,3,2]diazastannine-3,7-dicarbaldehyde (5). Column chromatography (DCM), MeOH precipitation, afforded the product as a cream white solid in 80% yields, m.p. 164-167 ºC (decomp.); MS (ESI+): 562 [M+H$^+$], 469, 299; ^{1}H-NMR (400MHz, $CDCl_3$): δppm= 0.79 (s, 3H, $H_{\alpha'}$), 1.01 (s, 3H, H_{α}), 3.33 (s, 3H, H_a), 5.48 (s, 1H, H_{10}), 6.2 (d, 2H, $H_{1,9}$, ^{3}J= 3.8 Hz), 6.72 (d, 1H, $H_{1'}$, ^{3}J= 8.25 Hz), 6.79 (d, 1H, $H_{9'}$, ^{3}J= 8.1 Hz), 6.91-6.94 (m, 3H, $H_{7',4',2'}$), 7.07 (d, 2H, $H_{2,8}$, ^{3}J= 3.8 Hz), 7.12 (dd, 1H, $H_{6'}$, ^{4}J= 1.5 Hz, ^{3}J= 7.6 Hz), 7.17 (td, 1H, $H_{8'}$, ^{4}J= 1.5 Hz, ^{3}J= 8.1 Hz), 9.14 (s, 2H, $H_{1a,9a}$); ^{13}C-NMR (100 MHz, $CDCl_3$): δppm= 3.66 (CH, C_{α}), 4.64 (CH, $C_{\alpha'}$), 35.2 (CH, C_a), 44.2 (CH, C_{10}), 114 (CH, $C_{9'}$), 114.2 (CH, $C_{1'}$), 115.2 (CH, $C_{1,9}$), 122.5 (CH, $C_{7'}$), 122.9 (Cq, $C_{4a'}$), 123.9 (Cq, $C_{5a'}$), 124 (CH, $C_{2,8}$), 126.3 (CH, $C_{4'}$), 126.6 (CH, $C_{6'}$), 127.1 (CH, $C_{2'}$), 127.5 (CH, $C_{8'}$), 137.5 (Cq, $C_{9a,10a}$), 137.9 (Cq, $C_{3'}$), 144.6 (Cq, $C_{9a'}$), 145.6 (Cq, $C_{10a'}$), 151.7 (Cq, $C_{3,7}$), 178.4 (Cq, $C_{1a,9a}$); ^{119}Sn-NMR (149 MHz, $CDCl_3$): δppm= -219.24; IR (KBr): ū(cm^{-1})= 2962, 2851, 1592, 1499, 1305, 1062, 788, 747, 755;

5,5-dibutyl-10-(10-methyl-10H-phenothiazin-3-yl)-5,10-dihydrodipyrrolo [1,2-c:2',1'-*f*][1,3,2]diazastannine-3,7-diyl)-*bis*(phenylmethanone) (6). Column chromatography (DCM), MeOH precipitation, afforded the product as a pink solid in 65% yields, m.p. 86-87 ºC (decomp.); HRMS (APCI +): Calcd. for $C_{44}H_{44}SnN_3O_2S$ [M+H$^+$] 798.2154, Found 798.2171;^{1}H-NMR (400MHz, $CDCl_3$): δppm= 0.71 (t, 3H, $H_{\delta'}$, ^{3}J= 7.32 Hz), 0.79 (t, 3H, H_{δ}, ^{3}J= 7.32 Hz), 1.10-1.19 (m, 2H, $H_{\gamma'}$), 1.27-1.39 (m, 4H, $H_{\gamma,\beta'}$), 1.47-1.55 (m, 4H, $H_{\beta,\alpha'}$), 1.73-1.77 (m, 2H, H_{α}), 3.34 (s, 3H, H_a), 5.52 (s, 1H, H_{10}), 6.22 (d, 2H, $H_{1,9}$, ^{3}J= 3.8 Hz), 6.74 (d, 1H, $H_{1'}$, ^{3}J= 8.3 Hz), 6.79 (d, 1H, $H_{9'}$, ^{3}J= 8 Hz), 6.91 (t, 1H, $H_{7'}$, ^{3}J= 7.5 Hz), 7.01 (d, 1H, $H_{4'}$, ^{4}J= 2 Hz), 7.03 (dd, 1H, $H_{2'}$, ^{4}J= 2 Hz, ^{3}J= 7.3 Hz), 7.09-7.17 (m, 4H, $H_{2,8,6',8'}$), 7.48- 7.52 (m, 4H, $H_{c'}$), 7.55-7.58 (m, 2H, $H_{d'}$), 7.91 (d, 4H, $H_{b'}$); ^{13}C-NMR (100 MHz, $CDCl_3$): δppm= 13.6 (CH, $C_{\delta'}$), 13.7 (CH, C_{δ}), 24 (CH, C_{α}), 24.8 (CH, $C_{\gamma'}$), 25.9 (CH, C_{γ}), 26.4 (CH, $C_{\alpha'}$), 27.2 (CH, $C_{\beta'}$), 27.3 (CH, C_{β}), 35.2 (CH, C_a), 44.7 (CH, C_{10}), 114 (CH, $C_{9'}$), 114.06 (CH, $C_{1'}$), 115.3 (CH, $C_{1,9}$), 122.4 (CH, $C_{7'}$), 123.2 (Cq, $C_{4a'}$), 123.7 (Cq, $C_{5a'}$), 124.1 (CH, $C_{2,8}$), 126.6 (CH, $C_{4'}$), 127 (CH, $C_{6'}$), 127.1

(CH, $C_{2'}$), 127.4 (CH, $C_{8'}$), 128.4 (CH, $C_{c'}$), 129 (CH, $C_{b'}$), 131.6 (CH, $C_{d'}$), 135.8 (Cq, $C_{a'}$), 137.7 (Cq, $C_{9a,10a}$), 137.5 (Cq, $C_{3'}$), 144.5 (Cq, $C_{9a'}$), 145.7 (Cq, $C_{10a'}$), 151.6 (Cq, $C_{3,7}$), 184.6 (Cq, $C_{1a,9a}$); ^{119}Sn-NMR (149 MHz, $CDCl_3$): δppm= -271.50 ppm; IR (KBr): ū (cm^{-1})= 2955, 2851, 1538, 1463, 1382, 1333, 1258, 1064, 887, 727, 697, 623.

(5,5-dimethyl-10-(10-methyl-10H-phenothiazin-3-yl)-5,10-dihydrodipyrrolo [1,2-c:2',1'-f][1,3,2]diazastannine-3,7-diyl)-*bis*(phenylmethanone) (7). Column chromatography (DCM), MeOH precipitation, afforded the product as a rose-white solid in 67% yields, m.p. 160-163 ºC (decomp.); MS (ESI+): 714.1 [$M+H^+$]; ^{1}H-NMR (400MHz, $CDCl_3$): δppm= 0.83 (s, 3H, $H_{\alpha'}$), 1.11 (s, 3H, H_{α}), 3.34 (s, 3H, H_a), 5.55 (s, 1H, H_{10}), 6.26 (d, 2H, $H_{1,9}$, ^{3}J= 3.8 Hz), 6.74 (d, 1H, $H_{1'}$, ^{3}J= 8.3 Hz), 6.79 (d, 1H, $H_{9'}$, ^{3}J= 8 Hz), 6.93 (t, 1H, $H_{7'}$, ^{3}J= 7.3 Hz), 7.03 (dd, 1H, $H_{2'}$, ^{4}J= 2 Hz, ^{3}J= 8.3 Hz), 7.06 (d, 1H, $H_{4'}$, ^{4}J= 2 Hz), 7.11-7.19 (m, 4H, $H_{2,8,8',6'}$), 7.49-7.53 (m, 4H, $H_{c'}$), 7.56-7.60 (m, 2H, $H_{d'}$), 7.92 (d, 4H, $H_{b'}$, ^{3}J= 8.5 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$): δppm= 4.1 (CH, C_{α}), 5.1 (CH, $C_{\alpha'}$), 35.2 (CH, C_a), 44.6 (CH, C_{10}), 113.9 (CH, $C_{9'}$), 114.1 (CH, $C_{1'}$), 115 (CH, $C_{1,9}$), 122.4 (CH, $C_{7'}$), 123 (Cq, $C_{4a'}$), 123.7 (Cq, $C_{5a'}$), 124.2 (CH, $C_{2,8}$), 126.4 (CH, $C_{4'}$), 126.6 (CH, $C_{6'}$), 127.1 (CH, $C_{2'}$), 127.4 (CH, $C_{8'}$), 128.3 (CH, $C_{b'}$), 129 (CH, $C_{c'}$), 131.6 (CH, $C_{d'}$),135.3 (Cq, $C_{a'}$), 137.5 (Cq, $C_{9a,10a}$), 138.4 (Cq, $C_{3'}$), 144.5 (Cq, $C_{9a'}$), 145.6 (Cq, $C_{10a'}$), 151.4 (Cq, $C_{3,7}$), 184.2 (Cq, $C_{1a,9a}$); ^{119}Sn-NMR (149 MHz, $CDCl_3$): δppm=-247.19; IR (KBr): ū(cm^{-1})= 2923, 2850, 1530, 1414, 1308, 1017, 850, 750, 677.

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